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TRIAL BURN PROTOCOL VERIFICATION AT A HAZARDOUS WASTE INCINERATOR

by

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16. ABSTRACT

This full and summary report presents the results of a series of field performance tests supported by EPA conducted to (1) verify EPA hazardous waste incinerator trial burn protocol by actual on-site use and (2) to document actual field incinerator performance on a typical operating, state-of-the-art incinerator destroying real-world toxic and hazardous industrial waste.

The results of EPA's testing series reported here showed a number of interesting features associated with modern industrial liquid and solid waste incineration technology. First, EPA's testing protocols were proven essentially workable in the field except for highly volatile and very low (eg. under 100-300ppm) concentrations of principle organic hazardous constituents. Secondly, this incinerator, the Hamilton County, Ohio Metropolitan Sewer District (Cincinnati MSD) unit essentially met current EPA regulatory policy except for inert particulates in most circumstances. The overall activity also quantified costs of conducting typical trial burns for this and similar units.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This full and summary report presents the results of a series of field performance tests supported by EPA conducted to (1) verify EPA hazardous waste incinerator trial burn protocol by actual on-site use and (2) to document actual field incinerator performance on a typical operating, state-of-the-art incinerator destroying real-world toxic and hazardous industrial waste.

The results of EPA's testing series reported here showed a number of interesting features associated with modern industrial liquid and solid waste incineration technology. First, EPA's testing protocols were proven essentially workable in the field except for highly volatile and very low (e.g., under 100 to 300 ppm) concentrations of principle organic hazardous constituents. Secondly, this incinerator, the Hamilton County, Ohio Metropolitan Sewer District (Cincinnati MSD) unit essentially met current EPA regulatory policy except for inert particulates in most circumstances. The overall activity also quantified costs of conducting typical trial burns for this and similar units.

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PREFACE

This program, funded through Rockwell International Corporation under a contract with the U.S. Environmental Protection Agency, IERL-Ci, was conducted by Midwest Research Institute. Overall program direction was provided by Mr. Donald Oberacker, the Project Officer for EPA/Cincinnati.

Dr. Earl Hansen, Mr. Steve Swanson, and Dr. G. Jungclaus of MRI directed the chemical analysis effort on the project and provided the analytical results. Dr. Ken Wilcox and Mr. G. Cobb of MRI directed the field sampling activity. A great deal of cooperation on the actual field work was provided Mr. John Trapp of the Cincinnati Metropolitan Sewer District and all of the operating personnel at the incinerator.

ABSTRACT

Field tests were undertaken at the Cincinnati Metropolitan Sewage District (MSD) hazardous waste incinerator for the purpose of verifying the Environmental Protection Agency's (EPA's) trial burn protocol and to conduct an environmental assessment. The incinerator tested was equipped with a rotary kiln rated at 55 x 10^6 kJ/hr and a cyclone furnace rated at 65 x 10^6 kJ/hr. Air pollution control was provided by a scrubber, an absorber, and a demister. Two types of waste were fired during the tests, one was a pesticide containing waste and the second was a high chlorine content waste. Test results indicated that a 99.99 percent destruction and removal efficiency (DRE) was achieved, as required by the Resource Conservation and Recovery Act (RCRA) regulations for the selected principal organic hazardous constituents (POHC). However, the incinerator did not meet the particulate standard of 180 mg/dscm nor the HCl removal efficiency of 99 percent. It is believed that the malfunction of the demister and the low pH of the absorber solution were the probable reasons for the higher particulate loading and the low HCl removal efficiency, respectively. Several recommendations have been made with respect to the trial burn protocol and the sampling and analysis procedures.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

DFTPP -- decafluorotriphenylphosphine
DRE -- destruction and removal efficiency
dscm -- dry standard cubic meter
EPA -- Environmental Protection Agency
FD -- forced draft
GC/MS -- gas chromatograph/mass spectrometer
grav -- gravimetric
HC -- hydrocarbons
HCCP -- hexachlorocyclopentadiene
HHV -- high heating value
MM5 -- Modified Method 5
MS -- mass spectrometer
MSD -- Metropolitan Sewer District
PEG -- polyethylene glycol
PIC -- product of incomplete combustion
POHC -- principal organic hazardous compound
QA/QC -- quality assurance and quality control
RCRA -- Resource Conservation and Recovery Act
RSD -- relative standard deviation
SASS -- source assessment sampling system
TCO -- total chromatographable organic
VOST -- volatile organic sampling train

SYMBOLS

C_{corr} -- corrected particulate concentration, mg/dscm
C_{actual} -- measured particulate concentration, mg/dscm
%C -- percent concentration of POHC in waste
H_i -- heat of combustion of POHC, Kcal/g
R_i -- residence time at ith run, sec
T_i -- combustion temperature at ith run, °F(°C)

SECTION 1

INTRODUCTION

Hazardous waste incineration regulations, as published in the Federal Register of January 23, 1981, include stipulations that require trial burns in incinerators. Therefore, the Environmental Protection Agency (EPA) prepared the "Guidance Manual for Evaluating Permit Applications"[1] that presents a draft protocol for conducting hazardous waste trial burns in keeping with the Resource Conservation and Recovery Act (RCRA) requirements. This project was directed toward verifying the trial burn protocol described in the EPA document. The incinerator selected for this project is the one operated by the Cincinnati Metropolitan Sewer District (MSD).

The objectives of the trial burn protocol verification program at the Cincinnati MSD incinerator were to:

- Verify the hazardous waste trial burn protocol.
- Evaluate incinerator effectiveness in destructing principal organic hazardous components (POHCs) contained in two liquid wastes.
- Assess the viability of current prescribed procedures in the draft EPA Guidance Manual, associated documents, and regulations.
- Evaluate typical operation of the incinerator.
- Conduct environmental assessments for the selected POHCs in the feed and effluent streams.
- Determine data relevant to the cost of conducting trial burns at similar incineration facilities.

Methodology used in the project was to review the Guidance Manual and prepare a test plan for a trial burn based on our interpretation of that manual and to conduct testing accordingly. This, of course, also included use of relevant sampling and analysis procedures stipulated in the manual and associated documents.[2,3]

Since the objectives of this project were focused on evaluation of the protocol and procedures, every effort was made to identify associated problems and to recommend solutions to overcome those problems. For this reason the emphasis of this report is on problems and deficiencies encountered in all phases of the work. Each of these problems is brought out to show why revisions are needed and to develop recommendations, so that the problems can be avoided or minimized in future trial burns.

The test plan developed for this project was far more extensive than might be required for a trial burn, since a major objective of the program was to evaluate and possibly improve the trial burn procedures. Furthermore, the EPA desired to conduct the test with two different and complex wastes and to investigate effects of different temperatures and residence times.

The conclusions and the recommendations of this project are presented in Sections 3 and 4, followed by five sections containing the description of the incineration facility, the test program, test results, evaluation of incinerator performance and environmental assessment, and evaluation of trial burn protocol and suggested revisions.

SECTION 2

SUMMARY

The principal objectives of this program were to verify the hazardous waste trial burn protocol in keeping with the RCRA requirements, to evaluate incinerator effectiveness in destructing POHCs, and to assess the viability of current prescribed procedures and performance parameters contained within EPA's incinerator regulations and associated documents.

DESCRIPTION OF FACILITY

The hazardous waste incinerator tested under this program is operated by the MSD and is located at 1600 Gest Street in Cincinnati. The incinerator is equipped with a rotary kiln rated at 55 x 10^6 kJ/hr and a cyclone furnace rated at 65 x 10^6 kJ/hr. Although the kiln is designed to handle solid or semisolid wastes, only liquid wastes were fired throughout the testing. The kiln and furnace are connected to a single combustion chamber to provide residence time for the combustion gas. Gases leaving the combustion chamber are quenched with water and passed on to a venturi scrubber for particulate removal and through a sieve tray caustic scrubber for HCl removal. From the sieve tray scrubber the gases are directed through a mist eliminator before they leave the stack. Liquid effluent from the scrubbing system goes to the treatment plant, and bottom ash is sluiced with water into a lagoon.

The incinerator operated quite well throughout the tests except for the frequent opening of a circuit breaker during the first series of tests because of a loose electrical connection, the deterioration of the stack's sound dampeners, and the breakdown of the mist eliminator at the top of the sieve tray scrubber prior to the second series of tests.

SAMPLING AND ANALYSIS PROGRAM

The sampling and analysis plan involved testing the incinerator while burning two different liquid wastes, one categorized as a pesticide-containing waste and the other as a high chlorine content waste. The two wastes were separately fired during two series of tests, one conducted during the week of July 19, 1981, and the other during the week of September 27, 1981. The first series of incinerator tests was conducted at three different temperatures (899, 1093, and 1316°C) and two residence times (1.5-2.2 sec and 3.3-3.7 sec), whereas the second tests were carried out at the same three temperatures but only at one residence time (1.5-2.2 sec). These conditions resulted in a total of nine test runs, six during the first series of tests and three during the second. The incinerator operating conditions were varied to establish the effect of temperature and residence time on POHC destruction and removal efficiency (DRE).

The test matrix required the sampling of the waste being burned, the fuel oil used, the ash, the scrubber effluent, the quench water, and the stack gases. The analysis of all samples taken was performed with the main objectives of determining the DRE for six POHCs, the particulate grain loading in the stack, the HCl removal efficiency, and the emission levels of volatile trace metals and CO, NO_x, and total hydrocarbons. Table 1 presents a summary of the sampling and analysis test matrix adopted for this program. The six POHCs selected for the two wastes were as follows.

POHCs Selected in First Waste	POHCs Selected in Second Waste
Chloroform	Trichloroethane
Carbon tetrachloride	Tetrachloroethane
Tetrachloroethylene	Bromodichloromethane
Hexachloroethane	Pentachloroethane
Hexachlorobenzene	Hexachloroethane
Hexachlorocyclopentadiene (HCCP)	Dichlorobenzene

The selection of the POHCs in the two wastes was based partly on the EPA ranking system, which takes into consideration the heat of combustion of the POHC and its concentration in the waste, and partly on other considerations. With the EPA ranking system, any POHC with a low heat of combustion is automatically assigned a high rank regardless of its concentration in the waste. Therefore, in addition to utilizing the EPA ranking system, POHCs were chosen because of their high concentration in the waste and because of their particular interest to either the EPA or the Cincinnati MSD. Hexachlorobenzene and hexachlorocyclopentadiene are POHCs which reflect these latter criteria.

RESULTS OF THE TEST PROGRAM

Based on the sampling and analysis effort, the DREs for the POHCs of interest, the HCl removal efficiency, the particulate concentration of the stack gas, and other results were obtained. These results are summarized in Table 2.

As shown in Table 2, the Cincinnati MSD incinerator achieved 99.99% DRE for the selected POHCs with the exception of bromodichloromethane at an operating temperature of 899°C (1650°F). Furthermore, test results indicate that, within the ranges of operating conditions tested, residence time and temperature had minimal effect on the DRE for the POHCs selected in this program based on the detection levels.

The particulate concentration limit of 180 mg/dscm was not achieved, probably because of the absence of the mist eliminator. The required HCl removal efficiency of 99% was also not achieved; but given the uncertainty of the sampling and analysis procedure for chloride determination, these data should be used with caution.

TABLE 1. SUMMARY OF SAMPLING AND ANALYSIS TEST MATRIX FOR TRIAL BURN AT CINCINNATI INCINERATOR

- Two liquid wastes (6 POHCs in each waste)
- Three operating temperatures--899°C (1650°F), 1093°C (2000°F), and 1316°C (2400°F)
- Two residence times
- Total of nine test days.

Sampling point[d]	No. of samples/test day	Total No. of samples/waste for each test day	Analysis[a]
S_1A/S_1B Waste	2 2-hr integrated samples and one 6-hr integrated sample. 1 other grab once each day.	4	6 POHCs, 12 metals,[b] Cl, HHV, vis., F.P., prox/ult
S_2A/S_2B Fuel oil	1 grab (mainly to verify absence of POHCs)	1	6 POHCs
S_3 Ash	4 grab (one for each section of sluice tank when plant dumps ash). Composite these grabs.	1	6 POHCs
S_4 Scrubber effluent	3 grab samples, composited to make one sample.	1	6 POHCs
S_5 Quench water	1 grab (mainly to verify absence of POHCs).	1	6 POHCs
S_6 Stack	· 4 EPA Method 5 trains (two simultaneous 6-hr trains and two 2-hr trains)	4	Particulate,[c] metals (As, Se, Hg) 6 POHCs, 2 PICs
	· 2 chloride trains.	2	Cl
	· 3 ORSAT runs for O_2 and CO_2	3	O_2, CO_2
	· Continuous monitoring for CO, O_2, NO_x, total HC	-	CO, O_2, NO_x, total HC
	· 1 integrated gas sample	1	6 POHCs, 2 PICs

---

[a] POHC analysis was conducted on all except the stack samples by two laboratories (MRI and Rockwell); the stack samples could not be analyzed by both labs since the sample quantities were insufficient.

[b] Twelve metals analyzed were Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Tl.

[c] Only selected train samples were analyzed for particulate, prior to POHC analysis.

[d] See Figure 2 of this report for identification of sampling point.

TABLE 2. SUMMARY OF INCINERATOR TEST RESULTS

Run No.	Pesticide-containing waste							High chlorine waste		
	1	2	3	4	5	6		7	8	9
Date	7/21/81	7/23/81	7/24/81	7/25/81	7/26/81	7/27/81		9/30/81	10/1/81	10/2/81
Waste feed rate (kg/min)	32.7	34.0	38.1	53.1	53.5	60.3		49.0	61.2	62.1
Chamber temperature (°C)	899	1093	1316	899	1093	1316		899	1093	1316
Residence time (sec)	3.3	3.7	3.4	2.2	1.8	1.7		2.3	2.0	1.5
Stack gas flow rate (dscm/min)	696	526	490	1020	1080	1010		976	1000	1160
O_2 Conc. in stack gas (%)	12.2	10.3	7.8	13.0	10.5	8.4		12.3	10.6	9.1
DRE for POHCs (%):[a]										
Chloroform	99.99	N/A	99.99	99.99	99.99	99.99	Trichloroethane	99.99	N/A	99.99
Carbon tetrachloride	99.99	N/A	99.99	99.99	> 99.96	> 99.9[d]	Tetrachloroethane	99.99	N/A	99.99
Tetrachloroethylene	99.99	N/A	99.99	99.99	99.99	> 99.97	Bromodichloromethane	99.97	N/A	99.99
Hexachloroethane	99.99	99.99	99.99	99.99	99.99	99.99	Pentachloroethane	99.99	99.99	99.99
Hexachlorobenzene	99.99	99.99	99.99	99.99	99.99	99.99	Hexachloroethane	99.99	99.99	99.99
Hexachlorocyclopentadiene	99.99	99.99	99.99	> 99.96	99.99	> 99.97	Dichlorobenzene	99.99	99.99	99.99
HCl removal effiency (%)[b]	98.5	99.4	99.7	98.5	98.1	83.8		99.5	98.7	95.3
Particulate Conc. (mg/dscm)[c]	N/A	327	N/A	N/A	146	N/A		2,230	1,710	1,130
Conc. of other pollutants										
CO (ppm)	0.6	3.6	8.2	16.8	7.0	3.0		3.3	8.9	10.6
NO_x (ppm)	122	146	118	137	136	135		132	145	130
HC (ppm)	2.1	3.3	1.8	1.1	0.7	1.3		0.5	1.7	0.6
Maximum Conc. of POHCs (μg/L):										
Scrubber effluent	< 5	< 5	< 5	< 5	< 5	< 5		< 7.5	< 7.5	< 7.5
Bottom ash	< 5	< 5	< 5	< 5	< 5	440		< 7.5	< 7.5	< 7.5

---

[a] DRE values are shown only to two decimal places, using 99.99 even if calculated value was > 99.99. Only the lowest value is shown.

[b] HCl based on excluding analysis of plug rinse. For Runs 7 to 9, values are estimates based on Cl analysis of MM5 trains.

[c] Particulate conc. adjusted to 12% CO_2.

[d] Due to low waste feed concentration and inadequate stack gas sample volume, DRE could not be calculated to more than one decimal place.

Sampling durations of 2 hr, using the Modified Method 5 sampling train (MM5)[5] should be adequate for detecting most POHCs even if they are destroyed at the 99.99% level, provided one sets a minimum concentration level of 1,000 ppm for the POHC selection criterion in the waste feed. In this program, with a minimum concentration level of 100 ppm, the results were adequate for calculating 99.99% destruction in almost all cases.

TRIAL BURN COSTS

One of the program objectives was to assess the manpower requirements for conducting a trial burn. Since the Guidance Manual does not clearly specify the number of runs or the duration of each run, we have estimated man-hour requirements for different levels of testing. It is estimated then one option covering three test runs of 2-1/2 hr duration each will require about 1,200 to 1,500 person-hours. Details of this option are contained in Section 9 of this report.

EVALUATION OF PROTOCOLS AND SUGGESTED REVISIONS

A major objective of this project was to identify problems in the protocol related to incinerator regulations and associated documents, and whenever possible to suggest improvements to the protocol and associated sampling and analysis methods.

Evaluation of Regulatory Aspects

A major difficulty encountered on this project was the acquisition and storage at the site of a sufficient quantity of waste to enable testing with the "same" waste throughout the test period. For the Cincinnati tests, this quantity turned out to be between 50,000 and 90,000 liters/day, depending upon the incinerator operating conditions and the heating value of the waste. If an incinerator operator is awaiting review of his trial burn application, then facilities for storage of these large quantities of waste will be required. One option for solving this problem would be to conduct trial burns on the waste(s) available at the site, directing trial burns toward the POHCs that are more difficult to incinerate, and allowing POHCs that are less difficult to incinerate to be burned without a trial burn.

Selection procedures for POHCs need to be clarified. In its present form, the EPA Guidance Manual[1] relies on the EPA ranking system, which emphasizes the heat of combustion and minimizes the importance of concentration. However, concentration becomes an important factor in identifying products of incomplete combustion (PICs), especially when proposed regulations require that they not be present at levels exceeding 0.01% of the original POHCs. Also, the aspects of identification/selection of PICs and the number of PICs to be examined require clarification.

The recent A. D. Little Sampling and Analysis Manual[2] prepared for EPA recommends that the permit writer select at least one POHC from the 20 most abundant organic components, and that other POHCs selected be present in the waste at 1,000 ppm or higher. This recommendation is not consistent with the ranking and selection methodology in the EPA Guidance Manual, and could therefore mean that compounds most difficult to incinerate would not be selected as POHCs if present at less than 1,000 ppm.

The EPA Guidance Manual for trial burns should address the problem of whether or not a trial burn must consist of three replicate tests. In its present form, the Guidance Manual implies that one test may be sufficient, whereas the A. D. Little manual implies that three tests may be necessary.

In addition to the trial burn requirement items, there are several limitations in the sampling and analysis plan procedures referenced in the EPA Guidance Manual and the associated SW-846[3] document. While many of these limitations are addressed in the A. D. Little Sampling and Analysis Manual, some problems still remain which merit resolution. These are summarized in the following subsection.

Evaluation of Sampling and Analysis Methods

The sampling protocol for the incinerator waste feed stream, scrubber effluent, and bottom ash, provides minimal information on how such samples should be taken during each test period. This is most critical for the waste feed samples. The most representative sample possible should be obtained; consequently, it is recommended that, wherever possible, an integrated sample be taken consisting of subsamples taken at 15-min intervals. This recommendation applies mainly, of course, to liquid wastes. It may not be necessary if the waste feed is known to be homogeneous and of consistent composition. For scrubber effluent and bottom ash, grab samples should be adequate.

Stack sampling was the most complex part of the actual field work, and the protocol at the time the tests were conducted was very limited, especially with regard to the specifics about the sampling train and the sampling time necessary. Much more detail on the Modified Method 5 train,[5] shown in Figure 1, is now available in the A. D. Little Sampling and Analysis Manual but is considerably different from the one in the EPA Guidance Manual. The latter manual needs to be revised.

Although the MM5 train was used in this project, several problems were encountered in the first series of tests. Slight modifications, however, eliminated most of these problems. The first problem was large amounts of condensate that collected in the impingers due to the high moisture gas stream from the wet scrubber. This caused excessive carryover or necessitated frequent interruptions to empty the impingers. For this reason, a large condensate collection bottle was incorporated in the second set of testing, and we recommend this arrangement for sampling such high moisture gas streams. Another problem involved the XAD-2 resin cartridges. Resin itself was not a problem, but the frit at the bottom tended to plug up, requiring changing of the cartridge. Based on discussions with others who have had similar problems, a small 3.175-mm (1/8-in.) hole was drilled in the frits, covered with glass wool, and repacked with the resin. This alleviated the problem. Others doing this type of testing should be prepared to take similar action or to do so before it becomes necessary in the field.

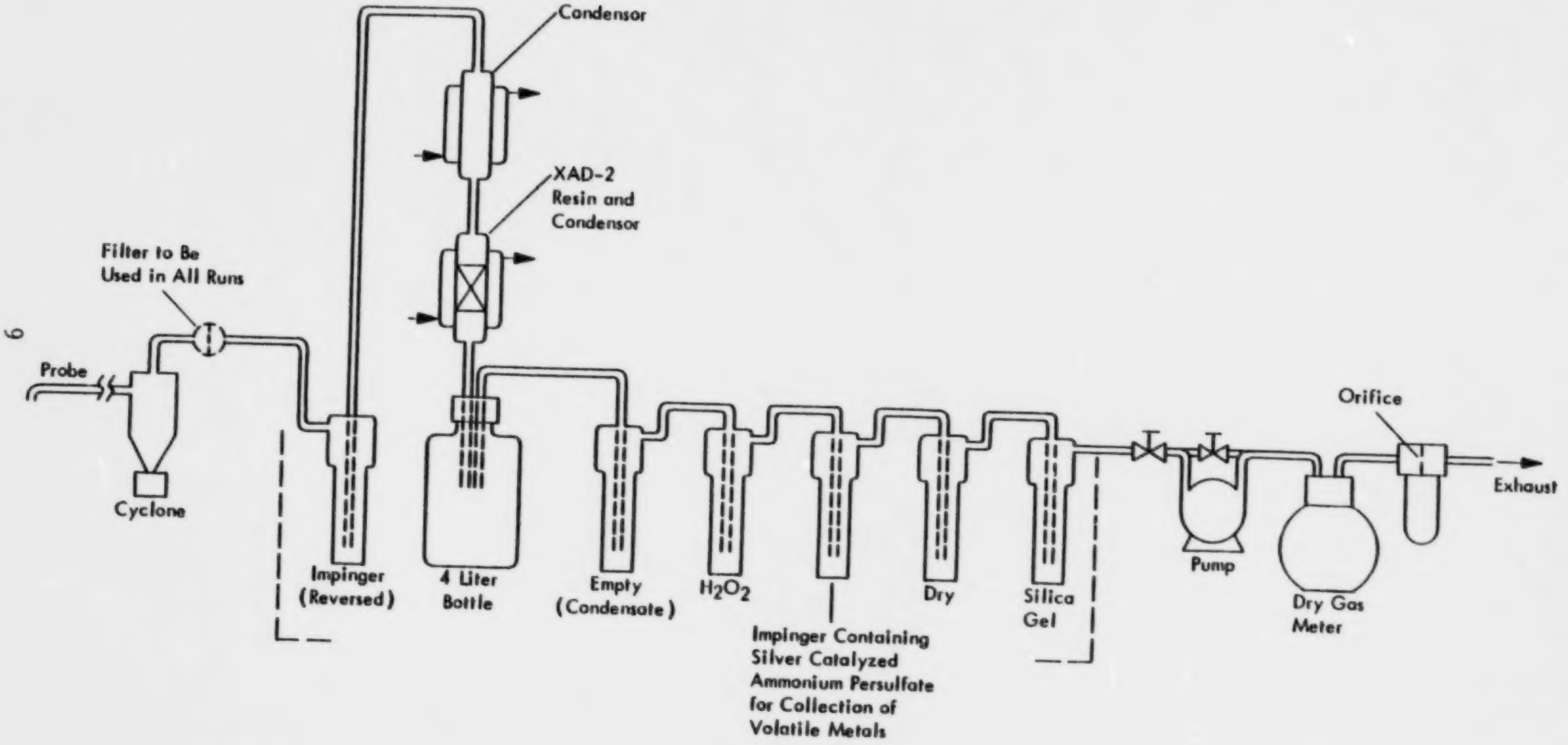

Figure 1. Schematic illustration of sampling train used at Cincinnati MSD incinerator tests.

Measurements of HCl in the first series of tests was done using the method in the EPA Guidance Manual. This technique might be suitable for determining HCl content of hot gas streams (e.g., municipal incinerator), but it is not suited for high moisture gas streams because the wet scrubber permits carryover of some liquid or solid particles that contain chloride salts, not necessarily HCl. These salts being counted as HCl will affect the analysis. The advantage of using the MM5 train, as recommended by A. D. Little, is that any Cl-containing particulate will be collected on the filter and will, therefore, not affect Cl analysis of the condensate and caustic impinger. Likewise, any droplets that enter the MM5 probe will most likely be evaporated, releasing any dissolved HCl and forming particulate from any chloride salts.

Protocol for integrated gas sampling is missing from the EPA Guidance Manual, but this is just as important a method of sampling as is the MM5 train because the analysis of these samples is the basis for calculating the DRE of any volatile POHCs. The recent A. D. Little manual discusses two options for taking such samples. The first requires the use of gas sampling bags, which are cumbersome to use in the field, require careful handling, and tend to leak. The second option involves sampling with 2-liter gas bulbs. However, the 2-liter bulbs take only grab samples, making reliance on them questionable for evaluating DRE. For these reasons, different procedures should be investigated for integrated gas sampling. One option is EPA Method 25,[4] which was used during our second series of tests. Another option is presented for consideration in Appendix K of this report. However, while this report was being written, EPA initiated work on a volatile organic sampling train (VOST) that will hopefully overcome the above problems.

In the analysis protocol, the most complex aspect was the waste feed analysis. In analyzing for volatile POHCs in the waste, the polyethylene glycol (PEG) method was used because the samples would not disperse in water. The EPA Guidance Manual does not address these details, and the A. D. Little document which mentions the PEG method as an option does not offer adequate details.

Analysis of waste feed samples for major constituents (non-POHCs) was very difficult. There is little information available on the procedures that may be necessary. The A. D. Little manual does recommend a "survey analysis" of waste feed samples to identify major types of organic compounds. Those analyses consist of Total Chromatographable Organics (TCO), Grav, infrared, probe MS procedures, and GC/MS. Only the latter two actually identify specific compounds, and both were tried on this program without total success in identifying the major organic components of the complex waste feed samples. Therefore, it appears that the survey analysis will be of limited usefulness and that it would be more worthwhile to carry out only the "directed analysis" to semiquantitatively determine all compounds present in the sample that are listed POHCs.

The determination of water in liquid wastes that are high in organic content was difficult. The methods specified in the protocol were found not to be applicable for such wastes, and it is recommended that water be determined by the Karl Fischer titration method.

Metals analysis of the waste feed samples presented another difficult problem, since the semisolid phase present in the samples could not be effectively digested by the specified techniques. The EPA presently is investigating and developing better digestion methods for such cases. In this regard, one could question the need for analyzing the waste for metals in a trial burn protocol where the emphasis is on POHCs.

Measurements of the emission of vaporous metals is discussed in the A. D. Little manual and is based on use of a special impinger in the MM5 train. However, it would seem logical to expect that some of these vaporous metals might be captured in the condensate on other impingers preceding the special impinger. Therefore, analysis of these components should be included.

It must also be noted that the A. D. Little manual shows that particulate from the MM5 train is to be extracted and analyzed for both metals and POHCs. It is our understanding that this means splitting the particulate sample, and analyzing one part for metals and the other for organics. More information on this and subsequent procedures is to be added to the A. D. Little manual.

The last problem relates to Cl analysis for determining HCl emissions, which was discussed above in terms of sampling limitations.

SECTION 3

CONCLUSIONS

Conclusions drawn from this work are given below, and each of them is closely tied to one or more of the program objectives stated in Section 2.

1. The Cincinnati MSD incinerator:

   a. Did achieve 99.99% DRE for the selected POHCs, with the exception of bromodichloromethane when operating at a temperature of 899°C (1650°F).

   b. Indicated that, within the ranges of operating conditions tested, time and temperature had minimal effect on DRE of the POHCs selected in this program based on the detection levels.

   c. Did not achieve the particulate concentration limit of 180 mg/dscm, probably because the demister had been removed from the scrubber.

   d. Did not achieve 99% HCl removal efficiency in most tests.

   e. Was adequately assessed for DRE of POHCs that were selected in this program, at the concentration levels present in the waste, using 2-hr sampling with the MM5 train.

2. Overall, trial burns can be carried out successfully using the most recent protocol, with the suggested changes and clarifications.

3. Storing sufficient waste of known composition for a trial burn may be a significant problem.

4. Several changes and clarifications are needed in the Guidance Manual and A. D. Little manual, as noted in various parts of this report and summarized in the following recommendations section.

SECTION 4

RECOMMENDATIONS

Several problems in the protocol and in the regulations were encountered in carrying out this project. All of these have been discussed throughout the report, and the more important of these are the basis for the recommendations presented below.

1. It is suggested that in performing trial burns, the emphasis be placed on the POHCs that are more difficult to incinerate.

2. Monitoring requirements need to include continuous O_2 monitoring, but delete air flow rate monitoring.

3. The Guidance Manual needs to address the problem of storing large quantities of waste of known composition, while awaiting review of a trial burn permit application.

4. The EPA should resolve the question of whether or not a trial burn must consist of three replicate tests.

5. Selection procedures for POHCs need to be clarified, defining whether or not a POHC can be selected that is present in a high concentration but easier to incinerate, and defining the lower concentration limit for POHCs (i.e., 100 or 1,000 ppm).

6. Selection of PICs, if required, should be based on examination of GC/MS data from the trial burn, rather than trying to predict the PICs that may be formed in the incineration of complex wastes.

7. Better methods need to be specified or developed for sampling of volatile POHCs in stack effluents.

8. The Guidance Manual should be revised to make it consistent with the A. D. Little manual, especially with regard to the stack sampling train.

9. Both the Guidance Manual and A. D. Little manual need to define the required frequency of sampling that is necessary, especially for liquid waste feeds.

10. If it is considered necessary in a trial burn, analysis procedures need to be developed for quantifying specific major compounds present in the waste (other than POHCs).

11. The A. D. Little manual should emphasize the "directed analysis" of the waste feed to specifically identify all potential POHCs that are present, rather than the "survey analysis" that is nonspecific, unless there is a need to predict PICs that may be formed.

12. EPA needs to clarify nomenclature relative to the determination of organically bound chlorine in the waste feed, since wastes might contain significant amounts of inorganic chlorine.

13. Several minor, but still important, additions or changes are needed in the Guidance Manual and/or A. D. Little manual as follows:

a. Work should continue on development of better digestion techniques for analysis of metals in waste samples.

b. There is a need to revise the method specified for determination of moisture in waste feed samples (use Karl Fischer titration).

c. The A. D. Little manual should specify that particulate samples (filter) are to be split in order to determine both metals and POHCs, and should specify how each part should be extracted and analyzed.

d. There is a need to develop methods for determining recovery efficiency of POHCs from solid substrates (e.g., spiking of filter and XAD resin samples during the analysis process).

e. EPA needs to better address sampling of high moisture content stack gases.

SECTION 5

FACILITY

The hazardous waste incinerator operated by the Cincinnati Metropolitan Sewer District is located at 1600 Gest Street in Cincinnati. As shown in the schematic in Figure 2 and in the photographs shown in Figures 3 and 4, this incinerator is equipped with a rotary kiln and a cyclone furnace. It is designed for a total heat release rate of 120 x 10^6 kJ/hr (114 x 10^6 Btu/hr) which is split as follows:

Rotary Kiln - 55 x 10^6 kJ/hr (52 x 10^6 Btu/hr)
Cyclone Furnace - 65 x 10^6 kJ/hr (62 x 10^6 Btu/hr)
Total - 120 x 10^6 kJ/hr (114 x 10^6 Btu/hr)

Although the unit does include a rotary kiln, solid or semisolid wastes are not being fed to the kiln. So far, it has been used primarily as a liquid injection incinerator, with liquid being fed into both the kiln and the cyclone furnace. The kiln and cyclone furnace are connected to a single combustion chamber that is 4.15 m diameter by 12.2 m high (13.5 ft diameter by 40 ft high) which provides residence time for the combustion gas. The temperature in this chamber is normally maintained at 982°C (1800°F).

Gases exiting the combustion chamber are immediately quenched with water and pass into the venturi scrubber and then flow upward through the sieve tray scrubbing tower. Liquid feed to the venturi scrubber and sieve tray scrubber is intended to be maintained at pH 6.0 (for HCl removal). The top of the sieve tray tower did contain a vane type mist eliminator, but this mist eliminator failed and had to be removed prior to the second series of tests (Runs 7, 8, and 9).

Cooled gases from the scrubber are exhausted through the induced draft (ID) fan into the stainless steel stack. Liquid effluent from the scrubbing system goes to the treatment plant, and bottom ash is sluiced with water out to a lagoon (see Figure 5).

The incinerator operated quite well during the tests, except for the problems cited below. The problems encountered during the first series of tests were frequent circuit breaker trips believed to be caused by a loose electrical connection and deterioration of the sound dampeners in the stack. Both of these problems were corrected prior to the second series of tests.

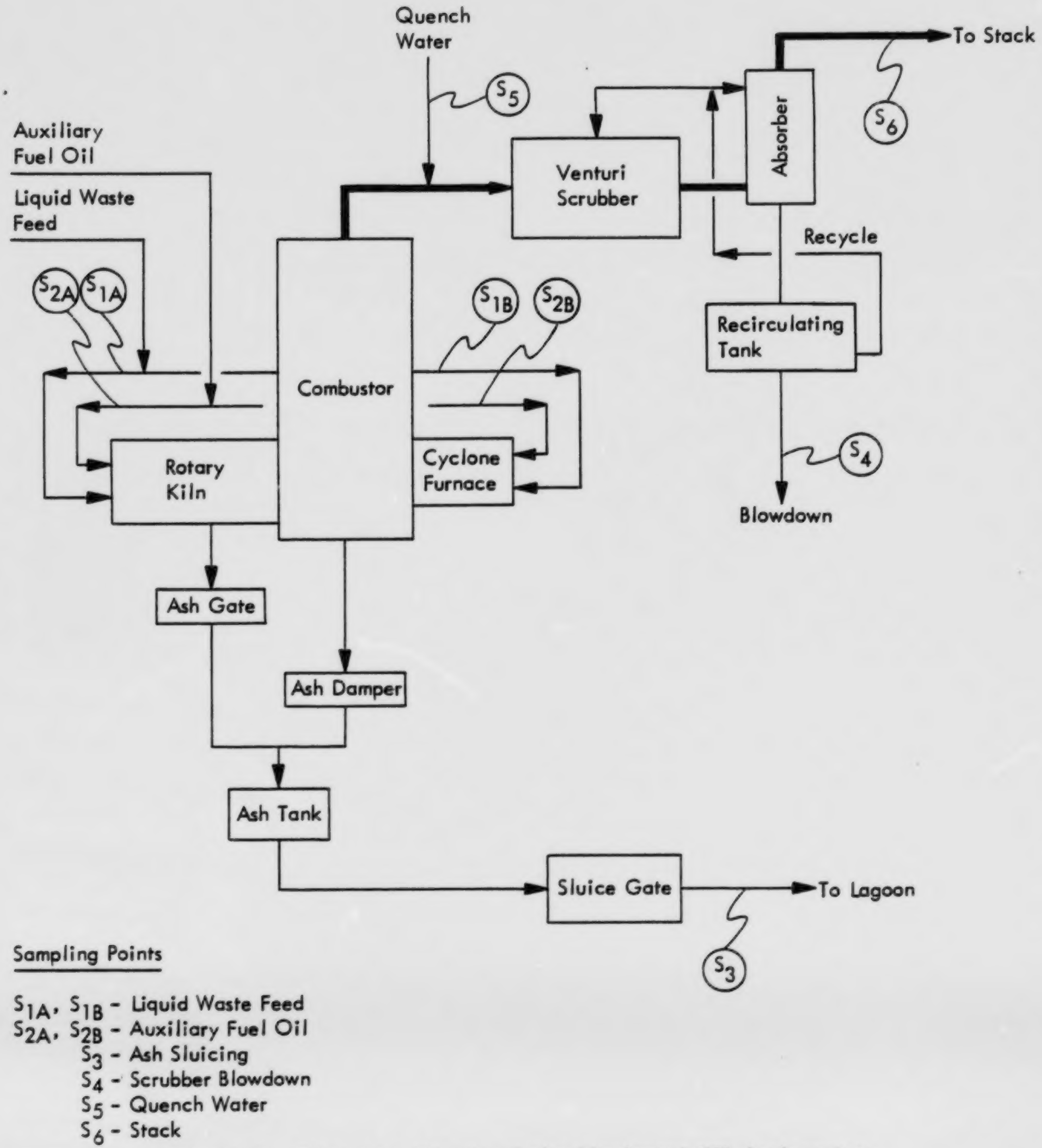

Figure 2. Schematic diagram of the Cincinnati MSD incinerator.

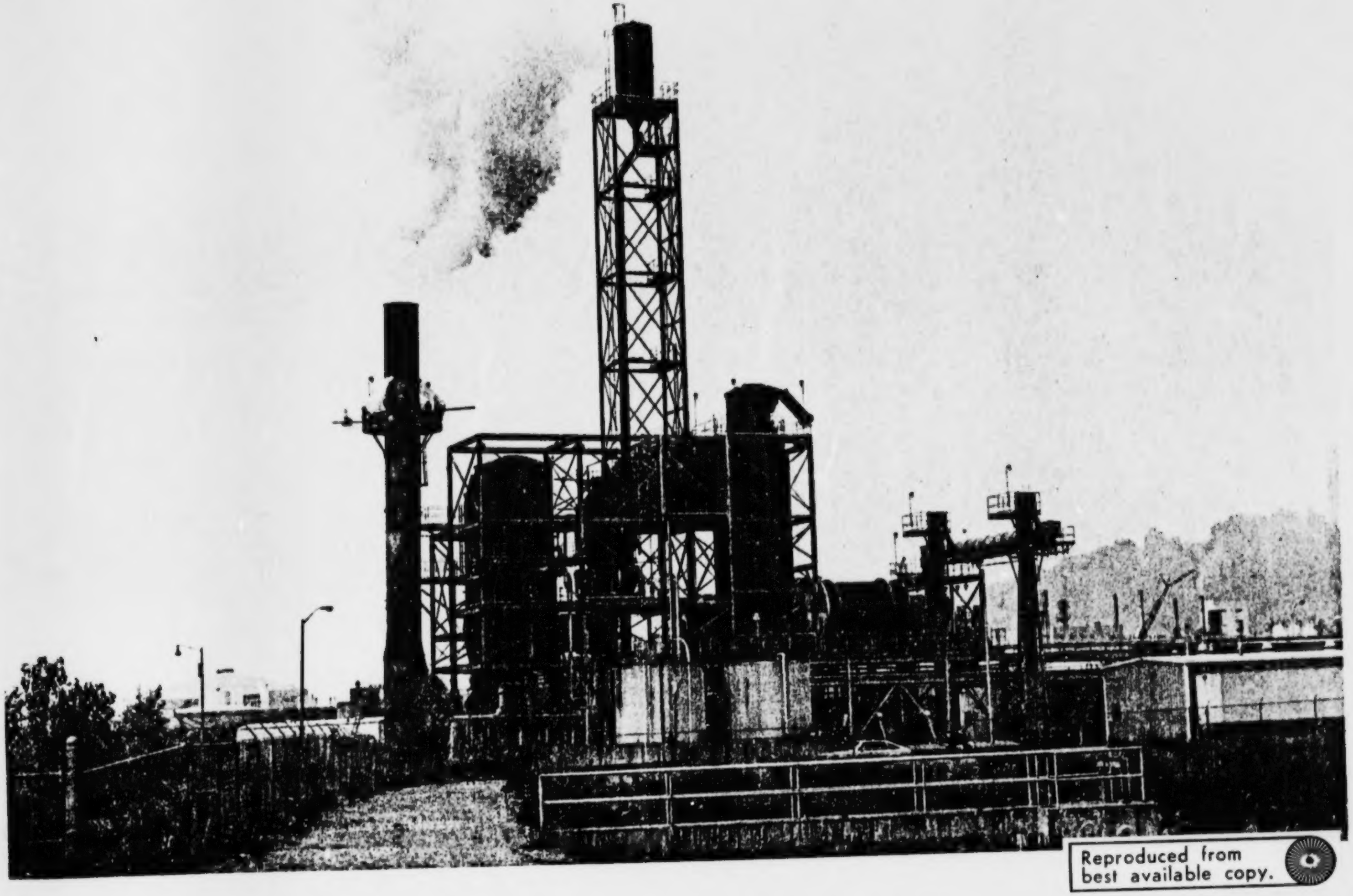

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Figure 3. The Cincinnati MSD incinerator facility.

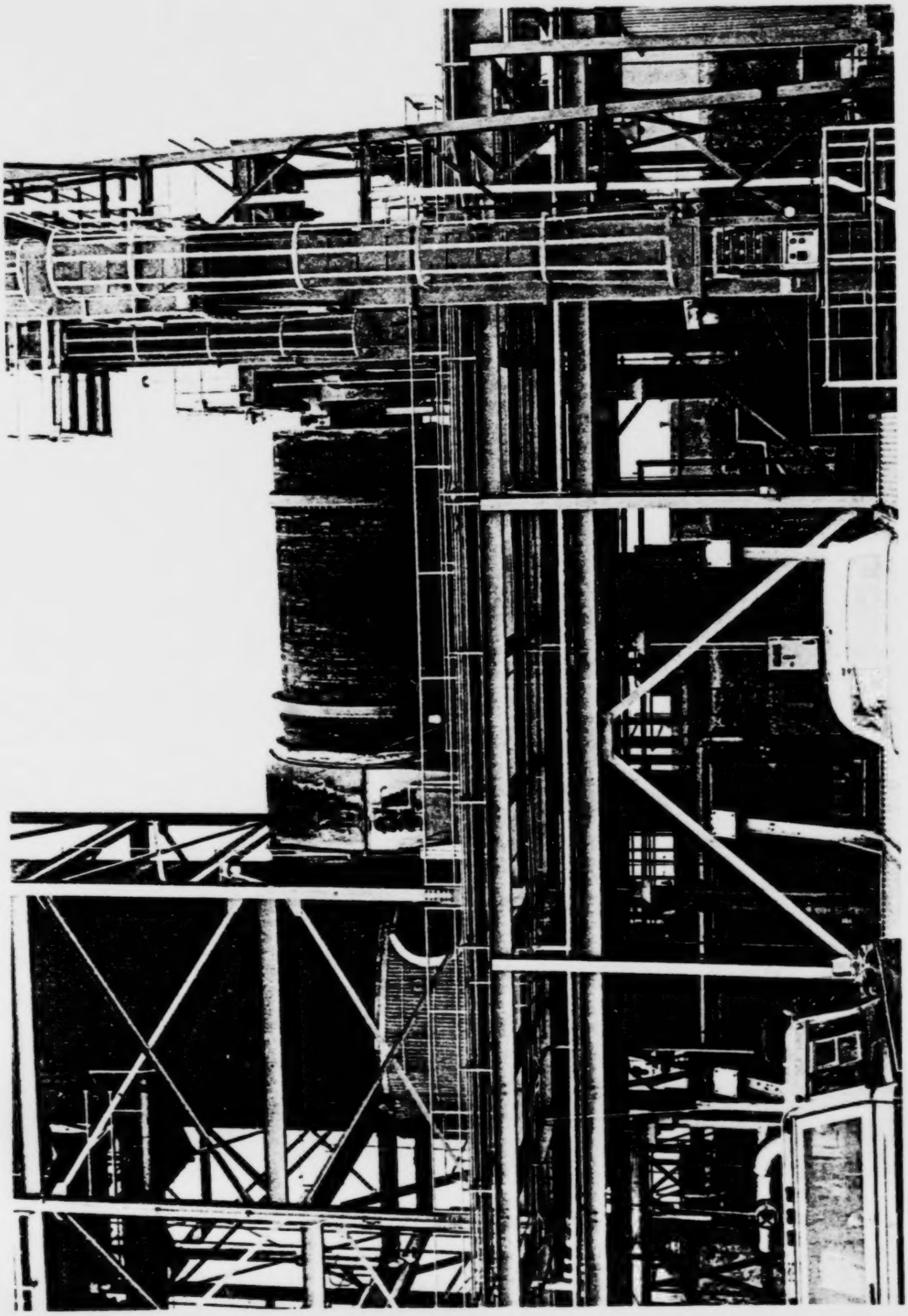

Figure 4. The MSD incinerator rotary kiln.

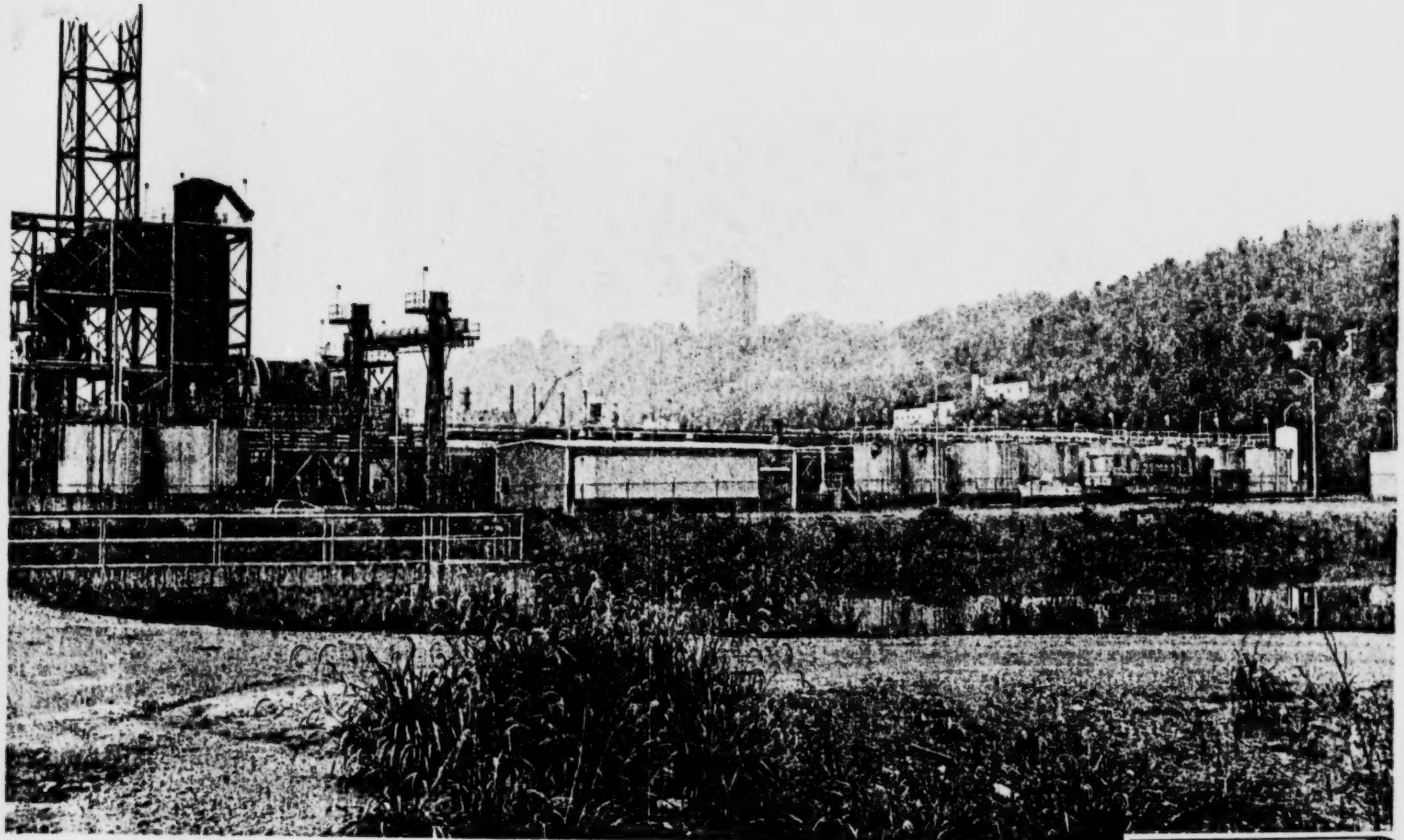

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Figure 5. Photo of incinerator, storage tanks, and lagoon (in foreground).

Before the second series of tests, the demister at the top of the scrubber failed and had to be removed. It is believed that removal of the demister prior to the second series of tests contributed to high particulate emissions. Also, during the second series of tests there was a problem in maintaining proper pH control of the recirculating solution.

The next section of this report describes the development of the test program and a discussion of the related protocol given in the Guidance Manual. A more detailed evaluation of the protocol is presented in Section 9.

SECTION 6

TEST PROGRAM

The protocol described in the EPA Guidance Manual[1] is fairly specific as to the sampling aspects of a trial burn; but with respect to the analysis, the procedures are poorly described. That is, the protocol states what streams are to be sampled and, to some degree, what they are to be analyzed for. However, it provides little information on the specified number of tests (replications), length of sampling time, specific sampling details (especially stack effluent), and analysis methods. In several instances, the analysis methods refer to SW-846,[3] but several of the techniques contained in the SW-846 document are not really applicable to the types of samples collected at a hazardous waste incinerator. A companion sampling and analysis manual, which was prepared by A. D. Little[2] under EPA contract during the time of the trial burn, provides a great deal of detail which is absent in the Guidance Manual.

Since the EPA desired to investigate the effect of temperature and residence time on destruction and removal efficiency and to test when firing two different wastes, it was decided that two series of tests would be carried out, as illustrated in Table 3, and that six principal organic hazardous components would be selected for each waste.

TABLE 3. SUMMARY OF TEST MATRIX

Waste A (6 tests)

Residence time	R_1			R_2		
Combustion temperature	T_1	T_2	T_3	T_1	T_2	T_3

Waste B (3 tests)

Residence time	R_2		
Combustion temperature	T_1	T_2	T_3

Note: During actual testing, the values of the variables were as follows:

R_1 = 3.3 - 3.7 sec
R_2 = 1.5 - 2.2 sec

T_1 = 899°C (1650°F)
T_2 = 1093°C (2000°F)
T_3 = 1316°C (2400°F)

From the results of this effort, these tests would be evaluated and sufficient information would be available for changing or improving the Guidance Manual, specifically its trial burn procedures.

In development of the test plan, it was originally intended also to investigate the effect of excess air, as well as temperature and residence time on DRE. However, it was later recognized that in this type of incinerator, temperature and residence time are the two basic independent variables and excess air is a dependent variable. That is, at any selected airflow rate (fan setting) and temperature (fuel/waste feedrate), the excess air level is fixed. Also, the excess air level decreases as the temperature increases. There seems to be a common misconception that excess air is an independent variable, which is not true. Thus, in this program, it was decided only to investigate effects of different temperatures and residence times on DRE. For all of the nine tests shown in Table 3, a specific sampling and analysis scheme was prepared, based on the Guidance Manual or interpretation thereof. This scheme is outlined in Table 4. The sampling points in Table 4 correspond to those identified in Figure 2. Details of the sampling at each of these points are discussed in the following sections.

STACK SAMPLING

Referring again to Table 4, it can be seen that in each test, the stack sampling apparatus consisted of four separate sampling trains, two of which sampled simultaneously for 6 hr while the other two sampled consecutively for 2-hr periods within the 6-hr period. The primary reason for this extensive sampling was to check the precision of the method and, perhaps more importantly, to determine the length of sampling time necessary to ascertain whether 99.99% DRE was, or was not, achieved. This is critical to any trial burn and is discussed further in the next paragraph.

No information is provided in the Guidance Manual on the duration of sampling. However, the detection limits of the analytical technique for POHCs (GC/MS) require collection of about 1 µg (assuming no unforeseen interferences). Therefore, it is possible to estimate the length of time required for sampling with a Modified Method 5 sampling train in order to collect 1 µg of a POHC, assuming 99.99% DRE and a concentration in the waste feed of 100 ppm. (The Guidance Manual implies that 100 ppm is about the lowest detectable concentration in a waste feed.) Such estimates indicate that the resulting concentration in the stack effluent should be at least 1 $\mu g/m^3$. If 1 m^3 must be sampled in order to collect 1 µg, and assuming a sampling rate of 0.0142 m^3/min (0.5 cfm), then the minimum sampling time is about 1.2 hr. Thus, the test plan included 2-hr sampling, and as a backup, 6-hr sampling.

In the first series of tests at the Cincinnati Metropolitan Sewer District incinerator, several problems were encountered with the MM5 train, but minor modifications eliminated most of these problems. Among these problems were the plugging of the frit that supports the XAD-2 resin, and the very large quantities of condensate emitted from a hot saturated gas stream leaving the scrubber. These problems and the modifications to solve them are discussed in detail in Section 9 of this report.

TABLE 4. TEST MATRIX FOR TRIAL BURN AT CINCINNATI INCINERATOR

- Two liquid wastes (6 POHCs in each waste)
- Three operating temperatures--899°C (1650°F), 1093°C (2000°F), and 1316°C (2400°F)
- Two residence times
- Total of nine test days

Sampling point	No. of samples/test day	Total No. of samples/waste for each test day	Analysis[a]
S_1A/S_1B Waste	2 2-hr integrated samples and one 6-hr integrated sample. 1 other grab once each day.	4	6 POHCs, 12 metals,[b] Cl, HHV, vis., F.P., prox/ult
S_2A/S_2B Fuel oil	1 grab (mainly to verify absence of POHCs)	1	6 POHCs
S_3 Ash	4 grab (one for each section of sluice tank when plant dumps ash). Composite these grabs.	1	6 POHCs
S_4 Scrubber effluent	3 grab samples, composited to make one sample.	1	6 POHCs
S_5 Quench water	1 grab (mainly to verify absence of POHCs).	1	6 POHCs
S_6 Stack	· 4 EPA Method 5 trains (two simultaneous 6-hr trains and two 2-hr trains)	4	Particulate,[c] metals (As, Se, Hg) 6 POHCs, 2 PICs
	· 2 chloride trains.	2	Cl
	· 3 ORSAT runs for O_2 and CO_2	3	O_2, CO_2
	· Continuous monitoring for CO, O_2, NO_x, total HC	-	CO, O_2, NO_x, total HC
	· 1 integrated gas sample	1	6 POHCs, 2 PICs

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[a] POHC analysis was conducted on all except the stack samples by two laboratories (MRI and Rockwell); the stack samples could not be analyzed by both labs since the sample quantities were insufficient.

[b] Twelve metals analyzed were Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, and Tl.

[c] Only selected train samples were analyzed for particulate, prior to POHC analysis.

The Resource Conservation and Recovery Act regulations of January 23, 1981, require 99.99% DRE for POHCs, 99% removal efficiency for HCl (for waste containing more than 0.5% chlorine), and a limit of particulate emissions to 180 mg/dscm (corrected to 12% CO_2). Determination of DRE was the primary focus of the two 2-hr and two 6-hr sampling trains. However, in order to determine particulate emissions, it was decided to select two or three of the 2-hr trains from both series of tests to quantify particulates; after this quantification of particulates, these samples were analyzed for POHCs. The Guidance Manual[1] does not show whether this scheme is permissible, but the recently issued manual by A. D. Little[2] makes it clear that the MM5 train can be used to determine particulates and POHCs. In addition, the A. D. Little manual shows that HCl can be determined as part of the same MM5 train. The Guidance Manual indicated that a separate midget impinger train is to be used to assess HCl emissions and this method was adopted for this test program. Unfortunately, the specified midget impinger train is subject to several problems, and these are discussed in Sections 7 and 9.

The MM5 train was used to quantify emissions of potentially vaporous metals (As, Se, Hg) in accordance with instructions in the Guidance Manual.

Finally, in addition to its use in assessing POHCs, the MM5 train was used to assess products of incomplete combustion. Neither the Guidance Manual nor the A. D. Little manual is specific about defining PICs, their identification or selection, or the number of PICs that need to be assessed. In preparing the test plan, it was proposed that two PICs be assessed. This was done, but involved considerable judgment. Since PICs require such judgment and interpretation in any trial burn, it is recommended that more clarification be provided by EPA in this area.

Another very important aspect of the POHC sampling is that several potential POHCs, referred to as "volatile" (e.g., CCl_4), will not be effectively captured by the MM5 train. No mention of this is made in the Guidance Manual. In carrying out the test plan, integrated gas bag samples were taken on each test day and analyzed for the volatile POHCs. Problems of leakage were experienced with these integrated gas bags. Therefore, in later tests, gas tanks (EPA Method 25) were also used. This aspect of sampling volatile POHCs is discussed in more detail in Section 9.

Although the quantification of POHCs via the gas bags and MM5 trains was the major aspect of the test plan, a further interpretation of the Guidance Manual led to the inclusion of additional stack sampling. That is, gas samples were taken each day to determine concentrations of CO_2 and O_2. Also, continuous monitoring of stack gases was done throughout each test to determine concentrations of CO, O_2, NO_x, and HC.

WASTE FEED

Sampling and analysis of the waste feed, which is critical to determining DRE, was designed in the test plan to obtain representative samples that coincide with the stack gas samples. On that basis, the waste feed sampling included one 6-hr integrated sample corresponding to the two simultaneous 6-hr stack sampling trains. Likewise, it included two 2-hr integrated samples corresponding to the two consecutive 2-hr stack sampling trains. A fourth waste feed sample was taken as a grab sample for comparison with the other three integrated samples. The term "integrated sample" refers to a waste sample composed of a mixture of equal volume subsamples taken into the same sample container over a short time interval once every 15 min. Taking integrated samples required that one additional person be on the test crew. The Guidance Manual contains no specifics on how and when waste samples should be taken. The required analyses of the waste samples as specified in the Guidance Manual include POHC analyses, and several other analyses such as metals, Cl^-, HHV, viscosity, flashpoint, and proximate and ultimate analysis. Results of these analyses are intended to help a permit reviewer evaluate an incinerator permit application, as explained in the Guidance Manual. Thus, they were included in the test plan.

One very important aspect of waste feed in a trial burn such as this one is that large quantities of waste are consumed rather rapidly. If a trial burn consists of more than one test day, large quantities of the same waste must be held in storage. Or if the intent is to burn the same waste throughout the test period, different wastes must be held in storage and blended in the same proportions each day. A great deal of effort went into this aspect of the testing at the Cincinnati MSD requiring the use of waste from a variety of sources. Typically, the waste feed rate was 50,000 to 90,000 liters/day (13,000 to 24,000 gal/day) during the time of testing. Considering this, it is recommended that the Guidance Manual and associated document address this aspect of trial burns.

FUEL OIL

The acquisition of one grab sample of fuel oil on each test day and analysis of selected grab samples of fuel oil for POHCs were included in the test plan. The purpose of this analysis was to ensure that the selected POHCs were not present in the auxiliary fuel oil used for the MSD incinerator.

QUENCH WATER

Quench water is used at the incinerator to cool the gases leaving the combustion chamber and this quench water also serves as makeup water to the gas scrubbing system. A grab sample of the quench water was taken each day for the same purpose as the fuel oil samples discussed above.

SCRUBBER EFFLUENT

Recycled scrubbing solution is automatically discharged from the recirculation tank on a semicontinuous basis (flow rate could not be determined). In developing the test plan, it was decided to obtain a grab sample of the scrubber effluent three times during each 6-hr test period. These three grab samples were later composited to yield one sample of scrubber effluent for each test day. The composited samples were analyzed for POHCs as specified in the Guidance Manual.

BOTTOM ASH

The term "bottom ash" is somewhat of a misnomer for the MSD facility because it implies a solid waste. The "solids" from the combustor and kiln at the MSD incinerator fall into a water-filled tank, and this tank is "sluiced out" with water once each shift. As a result, the bottom ash samples taken during each sluice were actually a small amount of ash in a large amount of water.

At the MSD incinerator, the ash tank has four compartments that are sluiced out in sequence. Therefore, a grab sample of the sluice liquid was taken as each compartment was sluiced. These four samples were then composited to form a single sample for each test day and was analyzed for POHCs. Since methodology for obtaining such samples is not contained in the Guidance Manual or associated documents, the method used was the only feasible one in this specific situation.

PROCESS DATA

During development of the test plan, it was obvious that detailed process monitoring, and cooperation of the operating personnel, was essential to a successful test program. Therefore, throughout each day of testing, all essential process data were recorded once every 15 min. Special emphasis was placed on monitoring waste feed rate, which is critical to calculation of DRE.

This discussion of the test plan was intended to provide the reader with an understanding of how the testing was carried out at the MSD incinerator. The test plan was developed in accordance with the Guidance Manual for the main purposes of evaluating the trial burn protocol (as presented in the Guidance Manual and associated documents), evaluating the incinerator performance, and producing recommendations for future trial burns. Test results are presented in the next section, and a discussion of the evaluations of those results follows in Sections 8 and 9.

SECTION 7

TEST PROGRAM RESULTS

Presentation of test results necessitates some discussion of sampling and analysis methods, details of which are the subject of a later section. Therefore, in this section, an attempt has been made to minimize discussion of sampling and analysis methods except as needed to present the test data and results as completely as possible. For ease in reading, only the summaries of the data are presented in this section; the detailed data on the results are given in the appendices.

Emphasis in this project centered on the determination of the destruction and removal efficiency of an incinerator for the POHCs. This is one of the principal objectives of a trial burn. The first part of the test program included the selection of the POHCs. An understanding of how and why the POHCs were chosen is helpful in following the test program results. Accordingly, the screening process leading to their selection for each of the two wastes used is discussed first.

SELECTION OF POHCs

Selection of POHCs requires a complete screening of the waste to quantify all potential POHCs that are present. A list of compounds screened for is given in Table 2-7 of the Guidance Manual.[1] This manual implies that analytical detection limits preclude compounds present below 100 ppm and the A. D. Little manual[2] implies selection of compounds present at ≧ 1,000 ppm. In either case, a screening analysis for a multitude of possible compounds in a complex mixture presents a formidable task because specific compounds must be identified and semiquantified (if present above 100 ppm). In the case of the tests performed for this program, the waste analysis was carried out by the procedures discussed herein. The results permitted identification of most potential POHCs, from which six were selected.

There is some question as to whether or not a sample of the waste must undergo screening analysis to select POHCs prior to a trial burn. It would be advantageous to do so if the operator wants to be assured that the waste contains certain POHCs during the trial burn or it may be required for inclusion in the trial burn permit application. Despite such obvious advantages, the problem in proceding with a screening analysis for POHC selection is that the entire quantity of waste needed for the trial burn must be held in storage after the sample is taken until the analysis results become available, the trial burn permit application is approved, and the test date has been set. If the incinerator burns a limited number of wastes with constant composition and ready availability, storage might not be necessary.

On the other hand, if the waste received at the facility is highly variable, storing all the waste necessary for the trial burn could tie up a large share of the facility's storage capacity for a considerable length of time.

In the case of the first series of tests at Cincinnati, about 360,000 liters (95,000 gal.) of pesticide-containing waste were accumulated during a period of about 1 month. Due to the periodic nature of the acquisition and storage process, a complete screening analysis was not possible until after samples of the waste were obtained during the actual testing. In the second series of tests, samples of waste held in four 95,000-liter (25,000-gal.) tanks were taken and underwent screening analysis during which time (~ 2 weeks) the waste was held in storage for the testing.

After receiving the results of the screening analysis, which semiquantified potential POHCs present in the samples, the POHCs were rank-ordered according to the method presented in the Guidance Manual, which is:

$$\text{POHC Rank} = (\%\ C) + \frac{100}{H_c}$$

where: $\%\ C$ = percent concentration of POHC in waste

H_c = heat of combustion of POHC, in kcal/g

Examination of the H_c values for POHCs reveals that if any POHCs that have a low H_c are present in the waste, they will have a high rank regardless of the fact that they may be present in very low in concentration. Apparently, the rationale for the ranking formula is that the POHCs with a low H_c are more difficult to destroy, and, therefore, should have a high rank and should be selected as the POHCs to be investigated in the trial burn. Other compounds with greater H_cs may not be selected even though they are present in much higher concentration. For this and other reasons, the selection of POHCs for the two wastes burned in the Cincinnati tests did not strictly follow a selection based only on rank, as explained below.

Results of the POHC screening analysis for the waste burned in both trial burns are shown in Table 5. It should be remembered that these two analyses were done at two different times.

For the waste burned in the first trial burn, the four highest ranking compounds were selected as POHCs. Two additional compounds were selected with less regard for their rank. Hexachlorobenzene was selected because of EPA's interest in this compound as a possible surrogate for polychlorinated byphenyls (PCB). Hexachlorocyclopentadiene (HCCP) was selected as one of the six POHCs because it is a pesticide of particular interest to the Cincinnati MSD and, of all the compounds identified, it was present at the highest concentration.

TABLE 5. RESULTS OF POHC SCREENING ANALYSIS

Rank	H_c[a]	$100/H_c$	Compound	Class[b]	Concentration range in waste burned in first trial burn (ppm)[c]	Calculated concentration in waste burned in second trial burn (ppm)
1	0.24	416.7	Carbon tetrachloride	V	1,600 - 9,800√	2,700
2	0.46	217.4	Hexachloroethane	SV	310 - 650√	8,100√
3	0.53	188.7	Pentachloroethane	SV	-----	8,900√
4	0.75	133.3	Chloroform	V	2,000 - 12,000√	7,300
5	1.19	84.0	Tetrachloroethene	V	1,300 - 1,800√	5,300
6	1.39	71.9	Tetrachloroethane	V	-----	10,400√
7	1.70	58.8	Methylene Chloride	V	1,000 - 7,300	6,700
8	1.74	57.5	Trichloroethylene	V	500 - 680	9,400
9	1.79	55.9	Hexachlorobenzene	SV	120 - 260√	< 100
10	1.99	50.3	Trichloroethane	V	1,000 - 13,000	32,700√
11	2.05	48.8	Pentachlorobenzene	SV	< 100 - 110	----
12	2.10	47.6	Hexachlorocyclopentadiene	SV	14,000 - 39,000√	300
13	2.12	47.3	Hexachlorobutadiene	SV	450 - 1,200	< 100
14	2.70	37.0	Dichloroethene	V	-----	150
15	3.00	33.3	Dichloroethane	V	1,000 - 5,100	6,100
16	3.38	29.6	Isodrin	SV	2,000 - 2,700	----
17	3.40	29.4	Trichlorobenzene	SV	< 100 - 110	----
18	3.44	29.1	Dichloropropene	V	-----	200
19	3.75	26.7	Aldrin	SV	180 - 300	----
20	4.51	22.2	DDT	SV	130 - 280	----
21	4.57	21.9	Dichlorobenzene	SV	1,100 - 5,100	1,200√
22	6.60	15.2	Chlorobenzene	V	1,600 - 4,600	6,200
23	6.92	14.5	Chlorotoluene	SV	1,200 - 1,700	1,000
24	7.34	13.6	Di-n-butylphthalate	SV	100 - 180	----
25	7.78	12.9	Phenol	SV	100 - 3,800	----
26	8.07	12.4	Toluene	V	3,100 - 5,100	8,900
27	8.07	12.4	MEK	V	1,600 - 3,700	2,400
28	8.29	12.1	Butylbenzylphthalate	SV	< 100 - 150	< 100
29	8.72	11.9	Bis(2-ethylhexyl)phthalate	SV	100 - 2,300	500
30	8.51	11.8	Dimethylphenol	SV	150 - 560	500
31	9.62	10.4	Naphthalene	SV	680 - 1,600	200
32	10.03	10.0	Benzene	V	200 - 1,000	4,000
				TOTAL	36,000 - 124,000	TOTAL 128,000

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[a] H_c = heat of combustion in kcal/g.

[b] Class designates whether the compound is a volatile (V) or semivolatile (SV). This designation reflects the analysis techniques for the waste feed samples, and the fact that subsequently, volatiles will most likely be detected in the integrated gas bag samples while semivolatiles will most likely be detected in the Modified Method 5 train samples.

[c] Concentration range shown is the lowest and highest concentration found in the six 6-hr integrated waste feed samples.

√ - Indicates compounds recommended as POHCs.

For the waste burned in the second trial burn, it can be seen in Table 5 that many of the potential POHCs were the same as those in the first trial burn. Therefore, selection of POHCs reflected an attempt to minimize duplication, and the basis for their selection was as follows:

- Hexachloroethane was selected because it had a high rank and was present at much higher concentration than in the first waste, so it could provide a good comparison of DRE for two different concentration levels.

- Pentachloroethane and tetrachloroethane were selected because of their high rank and the fact that they were not present in the first waste.

- Trichloroethane was selected since it was present at the highest concentration of all the compounds identified in the second waste.

- Even though it had a relatively low rank, dichlorobenzene was selected because it is a chlorinated aromatic compound and was present at higher concentration than was hexachlorobenzene (another aromatic) in the first waste.

Much later in the project, another POHC, bromodichloromethane, was selected as a POHC for the second waste. This compound was identified in the screening analysis but was not initially included because, in Table 2-7 of the Guidance Manual, it is not specifically listed but does fall into the listed category of "halomethane N.O.S." The reason for its later inclusion as a selected POHC is that it would have a high rank and, more importantly, is a probable precursor to the PICs that were selected.

In summary, the six POHCs selected for each of the two wastes were:

POHCs Selected

First Waste	Second Waste
Chloroform	Trichloroethane
Carbon tetrachloride	Tetrachloroethane
Tetrachloroethylene	Bromodichloromethane
Hexachloroethane	Pentachloroethane
Hexachlorobenzene	Hexachloroethane
Hexachlorocyclopentadiene	Dichlorobenzene

The above listed POHCs are those which were quantified in all the samples discussed in the test plan, and for which DREs were calculated.

TEST DATA AND RESULTS

The test plan required operating the incinerator at three different temperatures and two different residence times for the first series of tests, and at three different temperatures and only one residence time for the second series of tests. A summary of test conditions is given in Table 6. The three temperatures selected were 899°C (1650°F), 1093°C (2000°F), and 1316°C (2400°F). The two residence times could not be predicted accurately prior to the tests since residence time depends on flue gas flow rate measured during the test. Therefore, the longest residence time was that corresponding to fully closed dampers on the inlet of the two forced draft (FD) fans. Shortest residence time corresponds to FD fan damper openings of about 50% and resulted in a fuel combustion rate near the design limit of the incinerator (120 x 10^6 kJ/hr (114 x 10^6 Btu/hr)). After the tests, the residence times (as given in Table 6) were calculated from the combustion chamber volume (162 m^3 (5,726 ft^3)) and the calculated flue gas flow rate. That flow rate was calculated by using the measured stack gas flow rate (in dscm/min) and calculating a flue gas flow rate through the combustion chamber based on its outlet temperature (899, 1093, or 1316°C (1650, 2000, or 2400°F)) and an assumed moisture content of 5%. These calculations are reasonable approximations of the residence time in the combustion chamber but do not reflect additional residence time in the firing chambers (the rotary kiln or cyclone furnace). Thus, the times shown in Table 6 may be somewhat low, although the cyclone furnace could often be observed to be firing across the bottom of the combustion chamber.

Prior to the first day of testing, the incinerator was fired only on fuel oil to minimize any possible contamination of samples with some unknown wastes. Moreover, to conserve the subject waste, only fuel oil, at a low firing rate, was used at night between tests.

The general procedure, preceding each test, was to initiate firing of waste, increase fan openings if required, and select the desired operating temperature. The unit was then allowed to stabilize for 1 to 2 hr, with firing of fuel oil being reduced to the minimum possible. After the unit had stabilized at the desired conditions, sampling was started, and every attempt was made to keep the unit at those nominal conditions throughout each test period of several hours. The major problem at this point was frequent interruption of electrical power to the unit during the first series of tests. This, of course, necessitated immediate stopping of all sampling. Sampling was resumed after the circuit breakers were reset and the unit had been restarted and stabilized again. Constant monitoring of the process, and the close cooperation of the operators, was thus essential to this project.

Process Data

Throughout each test period, important process data were recorded every 15 min. These data have been summarized, for each test day, in Tables 7A and 7B.

One of the most important pieces of process data in the project was the quantity of waste burned during the sampling period. This information was obtained primarily from readings of the quantity (weight) of waste in the two feed tanks. They provided what is believed to be the most accurate measure of the amount of waste fed to the unit and did crosscheck very well with the waste flowmeters.

TABLE 6. SUMMARY OF TEST CONDITIONS AND POHCs SELECTED

	First waste					
Residence time (sec)	3.3 - 3.7			1.5 - 2.2		
Combustion chamber Temperature (°C)	900	1093	1316	899	1093	1316
Test No.	1	2	3	4	5	6

	Second waste		
Residence time (sec)	1.5 - 2.2		
Combustion chamber Temperature (°C)	899	1093	1316
Test No.	7	8	9

POHCs Selected

	Phase I	Phase II
Volatiles[a]	Chloroform Carbon tetrachloride Tetrachloroethylene	Trichloroethane Tetrachloroethane Bromodichloromethane
Semivolatiles[a]	Hexachloroethane[b] Hexachlorobenzene (HCB) Hexachlorocyclopentadiene (HCCP)	Pentachloroethane Hexachloroethane[b] Dichlorobenzene

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[a] Identification of volatiles and semivolatiles is important because they are analyzed by different methods. Also, in the stack effluent, the volatiles are quantified in the integrated gas bag samples whereas the semivolatiles are quantified from the Modified Method 5 train samples.

[b] Hexachloroethane was the only POHC selected in both wastes.

TABLE 7A. PROCESS DATA SUMMARY FOR RUNS 1 THROUGH 6

Parameter	Run No.					
	1	2	3	4	5	6
Nominal						
Combustion chamber temperature (°C)	899	1093	1316	899	1093	1316
Waste flow rate	Low	Low	Low	High	High	High
Measured						
Combustion chamber temperature (°C)	avg = 914	avg = 1080	avg = 1274	avg = 907	avg = 1118	avg = 1321
Total waste flow rate (Lpm)	37	32 to 37	41	50.7 to 67.4	41.3 to 64.4	48.8 to 76.5
Auxiliary fuel flow rate (Lpm)[a]	5.15	4.2 to 5.3	4.66	2.6 to 5.3	5.3 to 10	5.11 to 12.3
Stack excess oxygen (%)	avg = 12.6	avg = 9.1	avg = 6.8	avg = 13.0	avg = 11.0	avg = 8.75
Stack carbon monoxide (ppm)	zero	zero (1 surge to 18)	zero to 25	zero to 50	zero (1 surge to 6)	zero (1 surge to 4)
Kiln						
Auxiliary fuel flow rate (Lpm)[b]	1.9 to 2.84	1.1 to 1.5	1.5	1.1 to 2.7	1.3 to 11	1.3 to 4.5
Outlet temperature (°C)	904 to 1010	1093 to 1177	1204 to 1316	899 to 954	993 to 1271	1232 to 1371
Exit pressure (cm wc)	-1.3 to -2.0	-0.5 to 1.0	0.0 to -1.0	-0.25 to -1.3	0.0 to -1.5	-0.5 to -2.0
Cyclone						
Auxiliary fuel flow rate (Lpm)[b]	0.76 to 1.9	1.5 to 2.7	1.9	1.5 to 2.1	2.3 to 13	1.9 to 9.5
Outlet temperature (°C)	954 to 1104	1093 to 1204	1210 to 1354	899 to 1104	843 to 1171	1116 to 1260
Windbox pressure (cm wc)	-4.1 to -5.1	-2.54 to -3.8	-2.54 to -3.6	4.3 to 8.9	10 to 13	2.54 to 3.8
Combustion chamber pressure (cm wc)	-3.0 to -5.1	-2.0 to -3.3	-1.5 to -3.1	-1.8 to -3.8	-1.0 to -4.3	-1.3 to -4.1
Emission control						
Absorber tray pressure drop (cm wc)	12.7 to 15.7	12.2 to 16.8	10 to 11.9	16 to 25.4	19 to 25	21 to 25
ID fan inlet pressure (cm wc)	-91 to -102	-91 to -99	-89 to -94	-97 to -102	-114 to -119	-94 to -112
Main stack temperature (°C)	82 to 93	91 to 99	91 to 98	91 to 93	91 to 96	88 to 93
Miscellaneous						
Elapsed time	14 hr, 22 min	6 hr, 55 min	8 hr, 17 min	7 hr, 48 min	11 hr, 8 min	7 hr, 30 min
Down time	3 hr, 50 min	---	1 hr, 58 min	1 hr, 07 min	2 hr, 19 min	1 hr, 28 min
Run time	10 hr, 32 min	6 hr, 55 min	6 hr, 19 min	6 hr, 41 min	8 hr, 49 min	6 hr, 02 min

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[a] This is a time-weighted average flow rate calculated from tank level indicator calibrated by weight.

[b] These values were taken from flow rate indicators on the control panel. The flow rates were adjusted throughout the runs to maintain temperatures in the desired range.

TABLE 7B. PROCESS DATA SUMMARY FOR RUNS 7 THROUGH 9

Parameter	Run No.		
	7	8	9
Nominal			
Combustion chamber temperature (°C)	899	1093	1316
Waste flow rate	High	High	High
Measured (average values)			
Combustion chamber temperature (°C)	903	1092	1316
Total waste flow rate (Lpm)	50.57	62.42	67.42
Auxiliary fuel flow rate (Lpm)	3.8	3.8	6.4
Stack excess oxygen (%)	12.5	10.6	8.9
Stack carbon monoxide (ppm)	~ 0	8	8
Kiln			
Auxiliary fuel flow rate (Lpm)	1.9	1.9	3.0
Outlet temperature (°F)	~ 1060	1182	1407
Exit pressure (cm wc)	+ 0.25	0	0
Cyclone Furnace			
Auxiliary fuel flow rate (Lpm)	1.9	1.9	3.4
Outlet temperature (°C)	~ 1002	1025	1052
Windbox pressure (cm wc)	11	11	11.4
Combustion chamber pressure (cm wc)	- 1.5	- 1.5	- 1.5
Emission control			
Absorber tray pressure drop (cm wc)	~ 15	18	24
ID fan inlet pressure (cm wc)	- 112	- 114	- 124
Main stack temperature (°C)	74	77	77
Miscellaneous			
Elapsed time	9 hr:29 min	8 hr:20 min	7 hr:55 min
Down time	none	none	none
Run time	9 hr:29 min	8 hr:20 min	7 hr:55 min

Based on the monitoring of the weight of waste in the feed tanks, the time-weighted average feed rate of waste was calculated for each of the four periods during each test day when the four stack sampling trains were in operation. These waste feed rates, shown in Tables 8A and 8B, were used to calculate DRE. Also needed, of course, is the analysis of the waste feed, which is discussed in the next subsection.

Waste Feed Analysis Results

The waste feed samples were the subject of extensive analyses, as was outlined in the test plan. These analyses included:

- General analysis (HHV, Cl, viscosity, flashpoint, proximate/ultimate) and major constituents
- POHCs
- Metals

All samples were analyzed for POHCs, but only selected samples underwent the other analyses for waste characterization. Results from each of these analyses are discussed below.

General Analysis and Major Constituents--

General analysis results for the selected waste feed samples are tabulated in Appendix A and provide some important information. First, it appears that the waste used in Runs 1 through 6 varied considerably from day to day, as evidenced by heating values ranging from 11,510 to 23,137 kJ/kg (4,949 to 9,948 Btu/lb). Furthermore, it appeared to vary from hour to hour, as exemplified by Run 2 where the four samples ranged in heating value from 14,045 to 28,530 kJ/kg (6,039 to 12,267 Btu/lb). This variability seems to have occurred even though every effort was made to blend the waste equally for each test and the feed tank was continuously recirculated. One possible explanation for the variability is that the waste samples taken in Runs 1 through 6 were multiphase (two liquid layers and one semisolid layer), and that the proportions of each layer were different from sample to sample. Such multiphase samples makes aliquoting of samples for analysis more difficult. However, being aware of this, efforts were made to thoroughly shake the samples and aliquot them immediately. Comparing the general analysis results from Runs 1 through 6 with those from Runs 7 through 9, the latter results were more consistent, which corresponds with the observation that these samples were not multiphasic.

The general analysis results provide a second important piece of information. The waste used in Runs 1 through 6 was much higher in water content and much lower in Cl content (as expected) than was the waste in Runs 7 through 9. Identification of other major constituents is discussed in the following paragraphs.

TABLE 8A. WASTE FEED FLOW, RUNS 1-6

Run No.	MM5 train No.	Stack sampling time (min)	Total waste weight (kg) used during sampling itme	Time weighted average waste feed rate (kg/min)
1	M5(2)-1A	126	4,010	31.8
	M5(2)-1B	126	4,130	32.9
	M5(6)-1A	360	11,600	32.2
	M5(6)-1B	360	11,800	32.9
2	M5(2)-2A	126	4,040	32.0
	M5(2)-2B	126	4,480	35.5
	M5(6)-2A	360	12,200	33.8
	M5(6)-2B	360	12,200	33.8
3	M5(2)-3A	126	5,000	39.7
	M5(2)-3B	126	4,580	36.4
	M5(6)-3A	360	13,700	38.0
	M5(6)-3B	360	13,700	38.0
4	M5(2)-4A	126	6,820	54.1
	M5(2)-4B	126	7,080	56.2
	M5(6)-4A	288	15,300	53.0
	M5(6)-4B	287	15,200	52.8
5	M5(2)-5A	126	5,770	45.8
	M5(2)-5B	126	7,440	59.0
	M5(6)-5A	360	19,300	53.6
	M5(6)-5B	360	19,300	53.6
6	M5(2)-6A	126	5,860	46.6
	M5(2)-6B	126	9,230	73.3
	M5(6)-6A	360	21,700	60.2
	M5(6)-6B	360	21,700	60.3

TABLE 8B. WASTE FEED FLOW, RUNS 7-9

Run No.	MM5 train No.	Stack sampling time (min)	Total waste weight (kg) used during sampling time	Time weighted average waste feed rate (kg/min)
7	M5(2)-7A	126	6,220	49.3
	M5(2)-7B	126	6,170	49.6
	M5(6)-7A	360	17,600	48.9
	M5(6)-7B	360	17,800	49.4
8	M5(2)-8A	126	7,950	63.1
	M5(2)-8B	126	7,790	61.7
	M5(6)-8A	360	21,900	60.8
	M5(6)-8B	360	22,000	61.2
9	M5(2)-9A	126	7,670	60.8
	M5(2)-9B	126	7,830	62.1
	M5(6)-9A	360	22,400	62.1
	M5(6)-9B	360	22,400	62.1

Even though identification of major constituents is not directly required in the Guidance Manual and is not necessary for determination of DRE, it was felt that it would be desirable to characterize the waste to the fullest extent possible. Initially, it was thought that this would be rather simple, and that the gas chromatographic/mass spectrometric (GC/MS) analysis would probably indicate, semiquantitatively at least, the major organic components in the two wastes. Unfortunately, the problem was not so simple.

As discussed under the general analysis, one of the major components in the waste feeds was water, being much higher in the first waste than in the second. The screening analyses for POHCs (discussed earlier) identified numerous POHCs, but their total concentrations comprised only about 12% of the waste.

In an effort to characterize other major components, many different techniques were tried. These are discussed in detail in a memo attached as Appendix B. As summarized in that memo, none of the techniques identified any major organic constituents as being present at high concentration (> 5%). However, the techniques did provide quantification of several organic compounds and additional characterization of one of the waste feed samples as follows:

Constituent	Percent by Weight
Water	57
Volatile organic compounds	11
Semivolatile organic compounds	25
Nonvolatile organic compounds	2 (estimate)
Total	95

Quantification of specific volatile and semivolatile organic compounds is also contained in Appendix B.

Much of the investigation of major constituents focused on one of the samples of waste from the first series of tests. Because of this, only limited investigations of waste samples pertaining to the second waste (Runs 7 through 9) were done. This second waste was much lower in water content (~ 15%) than the first waste. Further, the probe mass spectrometric analysis indicated a much different composition for the second waste, and suggested the possibility of polyglycol ethers, which are common industrial chemicals.

The results obtained from these samples indicate that complete characterization and quantification of all compounds present in waste samples may be very difficult. It may also be expensive, especially if significant portions of the sample are not amenable to GC/MS analysis. Thus, some guidelines should be developed on the degree of characterization needed to accomplish the goals of the trial burn tests.

POHCs--

After the screening analysis for selection of POHCs, both MRI and Rockwell International analyzed each of the waste feed samples by GC/MS to quantify the six selected POHCs. These analytical results are tabulated in Appendix C. Intercomparison of the large amount of waste feed analysis results is somewhat difficult using the data tabulated in Appendix C. Therefore, these data have been presented graphically in Appendix D.

Like the general analysis results, the POHC analysis results indicate variability from day to day and between samples taken on the same day. Also, there is considerable variability between the MRI and Rockwell results. Variability was as much as a factor of 10 in some cases, but in general, the results between labs vary by a factor of two or less. It must be pointed out that both laboratories used the same analytical procedures and quantified against authentic standards. The quality assurance/quality control (QA/QC) procedures included spiking with surrogates and/or authentic standards to determine percent recovery and replicate analysis to assess precision.

The QA/QC procedures are discussed in more detail later in this section. As far as the waste feed samples are concerned, the QA/QC results by MRI and Rockwell showed good precision. They also demonstrated good accuracy with one exception. That is, the percent recovery (accuracy) determined by MRI was high (211%) for two of the semivolatile compounds in a waste feed sample from Run 8. This seems to be corroborated by Rockwell results that showed highly variable recoveries for semivolatile surrogates spiked into waste feed samples (i.e., chrysene-d12). Thus, there is reason to believe that waste feed analysis results for at least some semivolatiles in Runs 7 to 9 may be underestimated.

One important implication of the problem in semivolatile analysis results for the waste feed samples pertains to a comparison of 6 and 2 hr and grab samples taken each day. One of the reasons for taking these different samples was to determine if they were statistically different from each other or from day to day, and to determine if the MRI and Rockwell results were statistically different. However, since the precision of both laboratories was good, all of the waste feed analysis data were evaluated statistically in an attempt to answer the following questions:

1. For each POHC, are MRI results statistically significantly different from Rockwell results?

2. For each POHC, considering both MRI and Rockwell separately:

    a. Are the two 2-hr samples significantly different?

    b. Are 2-hr samples significantly different from 6-hr samples?

    c. Are 2-hr samples significantly different from corresponding grab samples?

3. For each POHC, considering both MRI and Rockwell separately:
   a. Are 2-hr samples significantly different from day to day?
   b. Are 6-hr samples significantly different from day to day?

As indicated above, the statistical evaluations were carried out for each POHC, but whenever it was found that the samples were significantly different for any one POHC it had to be concluded that the samples as a whole were significantly different.

Data on waste feed analyses, as tabulated in Appendix C, were used in the statistical analysis. This statistical analysis was done by two sided paired "T" tests, at the 90% confidence level.

For the first question above, comparing MRI and Rockwell, it was found that there was a statistically significant difference between the results from the two laboratories for three of the POHCs in the first waste and for all six POHCs in the second waste. Thus, it must be concluded that results from the two laboratories on these waste samples were statistically different. Such interlaboratory variations are not uncommon and anyone conducting a trial burn must be aware that results from different laboratories will not be exactly the same. Hopefully, the variability between laboratories found for these particular samples will serve as a guide to how wide the variability may be, as is shown graphically in Appendix D.

Considering the above, the results from MRI and Rockwell were evaluated separately to answer the second question. This second question was directed to comparison of sample types. In comparing the 2-hr A samples with the 2-hr B samples, it was found that there was no significant difference for either laboratory, except for one POHC (hexachloroethane) in the MRI data. However, the reason that it could not be shown that they were different is that the standard deviation of differences between each pair of samples was large, and the sample size was small (i.e., six samples and three samples).

Another comparison that was made was directed to 2-hr A samples versus 6-hr samples, and 2-hr B versus 6-hr. In these cases, it was found that there were always at least two POHCs for which the samples were significantly different. It was also found that there were three POHCs that were significantly different when comparing grab samples with the corresponding 2-hr sample. Based on these findings, it must be concluded that the different types of samples are different. The most important ramification of this finding is that the most representative possible sample must be taken of the waste, corresponding to the stack sampling period, and that a few grab samples (e.g., three) taken during that period may not adequately represent the waste fed to an incinerator during the stack sampling period (e.g., 2 or 6 hr).

Another question that it was hoped could be answered was, were there significant differences between the waste fed to the incinerator from day to day? However, this statistical analysis for each type of sample could not be carried out because samples taken on each day were not analyzed in replicate.

Metals--

One of the objectives of the test plan was to analyze the waste feed samples for 12 specific metals according to the Guidance Manual. Results of these analyses are contained in Appendix E. Since the samples contained both a liquid and a semisolid phase, it was originally intended that both phases would be analyzed in all samples, especially since it would be expected that metals might be present predominantly in the solid phase. However, complete digestion of the semisolid phase, necessary to carry out the analyses, turned out to be very difficult, even using more severe digestion methods than those as given in the A. D. Little manual. Therefore, the semisolid phase was analyzed only on the 6-hr waste feed samples and there is still some question as to whether the digestion was entirely complete. It is our understanding that development of more appropriate digestion techniques is currently under way by EPA.

Examination of the data in Appendix E shows, as expected, that the solids contained much higher concentrations of some metals (e.g., Ba, Cr, Pb). Of the three potentially vaporous metals (As, Hg, Se), the concentration of Hg in the waste feed was about the same in Runs 7 through 9 as in Runs 1 through 6, whereas the concentration of As and Se in the solid phase was much lower in Runs 7 through 9.

Stack Effluent Test Results

Stack sampling and sample analysis comprised the largest part of the work performed in this test program and are paramount to the determination of DRE. The sampling and analysis of stack effluents was intensive and involved determination of several constituents. The results of the sampling effort and the associated sample analysis are described in the next subsections as follows.

- Stack effluent data
- POHCs and DRE
- Products of incomplete combustion
- Cl^-
- Particulates
- Vaporous metals
- HC, CO, NO_x, O_2

Stack Effluent Characteristics--

One of the more important variables to be determined from stack testing is the stack flow rate, since it must be known in order to use other analysis data to calculate emission rates for specific pollutants and to calculate DRE. The stack effluent data measured by each of the four sampling trains used on each test day, have been summarized in Appendix F. The primary use of these data was to calculate the DRE of the POHCs and to determine the Cl removal efficiency, which are discussed in subsequent sections. These data show that the moisture content of the stack gas was quite high, ranging from 36 to 53%. Thus, about one-third to one-half of all the stack effluent was water vapor that originated mainly from the quenching and scrubbing of the combustion gases. This high moisture content led to some problems in the stack sampling trains and required some change in the sampling train prior to Runs 7 through 9. These problems are discussed in Section 7.

It should be noted that the oxygen level decreases as combustion temperature increases. For example, the oxygen level was 15.6% in Run 1 (899°C (1650°F)) and decreased to 8.1% in Run 3 (1316°C (2400°F)). Decreasing oxygen level with increasing temperature would be expected, but it may not always be understood that the oxygen level could not have been changed in any run without also changing the temperature. The point here is that excess air (oxygen) is not an independent variable.

An examination of the data summarized in Appendix F reveals some variability in the measured stack flow rate (actual m^3/min) among the four tests on any given day. Since the 2-hr sampling trains operated over different periods, this is not surprising. Because the two 6-hr trains operated simultaneously, they should yield the same flow rate and in fact do show close agreement, except for Run 4. The anomalous result in Run 4 is believed to be linked to the termination of Run 4 due to a plant shutdown after it was about 80% completed. Despite this problem, the samples from this run were analyzed and the results are included in Appendix F of this report.

POHCs and DRE--

Modified Method 5 sampling trains, of which four were used on each test day, each included four components (probe rinse, filter, XAD-2 resin, and condensate) to be analyzed for the six POHCs. Each of these components was extracted, and the combined extracts (with certain exceptions explained herein) were analyzed according to the techniques discussed in Section 7.

In addition to the MM5 trains, an integrated gas bag sample was taken on each test day and analyzed for the volatile POHCs, which may not effectively be collected by the MM5 trains (XAD-2 resin). Some of these gas bag samples leaked and were flat when returned from the field, even though they were checked for leaks prior to use. Therefore, in the later tests (Runs 7 through 9), both integrated gas bag samples and gas samples collected in 4-liter stainless steel tanks (EPA Method 25) were obtained at a low flow rate for a period of about 1 hr. Both were analyzed for the selected POHCs (i.e., the three volatile POHCs).

Analytical results for the above samples, as well as other results, to be discussed later, are tabulated in Appendix G. These data were then used, along with corresponding stack sampling data and waste feed rate and analysis data, to compute the DRE for each POHC. The DRE for each POHC in each test was calculated based on the individual analysis result for the associated waste feed sample.

The DRE calculations were made according to the method in the Guidance Manual. An example calculation is shown in Table 9. DRE calculation results for each test are contained in Appendix H and are summarized, as ranges, in Table 10. It should be noted that all DRE calculations were based on the MRI analysis of the waste feed samples, since only MRI analyzed the stack samples. An examination of the data in Appendix H shows that a DRE of 99.99% was achieved in almost all cases. Most of the cases where 99.99% could not be shown were due to an inadequate amount of sample, so the result had to be expressed as a "greater than" value (e.g., > 99.9%). The only exception, where it was clear that 99.99% was not achieved, was in Run 7 for bromodichloromethane. (Run 7 was at the lower temperature of 899°C (1650°F).)

In Runs 5 and 6, the DRE for carbon tetrachloride and tetrachloroethylene had to be expressed as a greater-than number, which was not above 99.99%, because the limited quantity of sample in the gas bags did not permit a sufficiently low detection limit.

Comparison of analytical results for the integrated gas bags and the stainless steel cylinders from Runs 7 and 9 showed that the stainless steel tanks contained much higher concentrations of trichloroethane. Use of the higher values in calculating DRE still showed a DRE of 99.99% or greater, but does give evidence that a more rugged and reliable sampling method is needed for volatile POHCs.

One of the most interesting aspects of the DRE data is that there was little evidence that the DREs were affected by the different temperatures or residence times, except for bromodichloromethane. As far as residence time is concerned, this may not be surprising since even the lowest value was relatively high (1.5 sec). However, it is surprising that a high DRE was achieved even at the lowest temperature of 899°C (1650°F) for these selected POHCs, which have a relatively low heat of combustion and are, therefore, considered difficult to destruct. (Combustion chamber temperature during each run is given in Tables 7A and 7B; presented earlier.)

As mentioned, in most runs the four components of each train were extracted and then combined for POHC analysis by GC/MS. In two runs (Runs 5 and 8) the components in one of the 6-hr trains were analyzed separately in an attempt to identify how the POHCs were distributed among the four different components of the sampling train. However, this distribution was not revealed because all analysis results were "less than" values.

TABLE 9. EXAMPLE CALCULATION OF DRE FOR ONE POHC

Measured values

Waste feed rate	49,000 g/min
Concentration of POHC in waste feed sample	4,200 μg/g
Stack flow rate	954 dscm/min
Quantity of stack gas sampled in train	2.89 dscm
Quantity of POHC found in sampling train	< 1 μg

Calculate POHC input:

$$(49{,}000\ \text{g/min})(4{,}200\ \mu\text{g/g})(10^{-6}\ \text{g}/\mu\text{g}) = 210\ \text{g/min}$$

Calculate POHC output:

$$(954\ \text{dscm/min})(< 1\ \mu\text{g}/2.89\ \text{dscm})(10^{-6}\ \text{g}/\mu\text{g}) = < .0003\ \text{g/min}$$

Calculate penetration and DRE:

$$\%\ \text{penetration} = \frac{< 0.0003\ \text{g/min}}{210\ \text{g/min}} \times 100 = < 0.0001\%$$

$$\text{DRE} = (100) - (< 0.0001) = > 99.9999\%$$

Note: Example is from Run 7, MM5 train No. M5(6)-7A.
POHC was pentachloroethane.

TABLE 10. RANGE OF DRE RESULTS AND FRACTION (μg/g) of UNDESTRUCTED POHCs

POHC	DRE (%)	μg of Undestructed POHC/g of POHC in the feed
	Runs 1 through 6	
Chloroform	99.998 - 99.9997	20 - 3
Carbon tetrachloride	> 99.9[a] - 99.999	< 1,000 - 10
Tetrachloroethylene	> 99.97[a] - 99.999	< 300 - 10
Hexachloroethane	> 99.99 - > 99.999	< 100 - < 10
Hexachlorobenzene	> 99.99 - > 99.999	< 100 - < 10
Hexachlorocyclopentadiene	> 99.96[b] - > 99.9999	< 400 - < 0.2
	Runs 7 through 9	
Trichloroethane	99.985 - > 99.99996	150 - < 0.4
Tetrachloroethane	> 99.9997 - > 99.9998	< 3 - < 2
Bromodichloromethane	99.97 - 99.996	300 - 400
Pentachloroethane	99.9994 - > 99.9999	6 - < 1
Hexachloroethane	> 99.999 - > 99.9999	< 10 - < 1
Dichlorobenzene	> 99.99 - > 99.999	< 100 - < 10

[a] DRE could only be expressed as > 99.9% or > 99.97% because inadequate sample was available for analysis from the integrated gas bag.

[b] DRE could only be expressed as > 99.96% because the concentration of compound in one waste feed sample was quite low (90 ppm).

Another aspect of the POHC analysis of the trains was that certain selected 2-hr trains were first used to determine particulate emissions. This means that the probe rinse was evaporated and weighed, and the filter desiccated and weighed, prior to their extraction for POHC analysis. It was not possible to determine if the subsequent POHC analysis was affected because, again, the results for both the affected train and its unaffected counterpart were "less than" values.

In summary, the DRE results from these tests led to four important conclusions.

- The incinerator was shown to achieve a DRE of 99.99% in almost all cases; possible exceptions are noted herein.
- DRE did not appear to be affected over the range of temperatures and residence times tested for all POHCs except bromodichloromethane.
- 2-hr sampling periods are adequate for most cases and marginal in some cases.
- The method for sampling volatile POHCs needs to be carefully selected.

PICs--

Measurement of PICs was included in the test plan for two reasons:

- PIC measurement is specified in the interim final regulation published January 23, 1981.
- The proposed regulations, published January 23, 1981, will require that emission of PICs not exceed 0.01% of the mass input of POHCs.

Although the proposed regulation is specific about the allowable emission of PICs, it is unclear about the definition of a PIC and how they are to be chosen or identified. It might be possible to predict the PICs that could result from combustion of a relatively simple waste, but such a prediction would be very difficult for wastes as complex as the two burned in these tests. Therefore, the approach used here was to carefully examine the GC/MS analysis data from the stack effluent samples (i.e., integrated gas bags and MM5 trains) in order to identify two major compounds that could be products of incomplete combustion. However, this identification was limited only to those compounds (potential POHCs) listed in Table 2-7 of the Guidance Manual which were not detected in the original waste (i.e., < 100 ppm).

There is an important point here, in that it was assumed that a PIC must be on the list of POHCs. To do otherwise would expand analysis requirements, and would seem to go beyond the intent of the regulations. But even this interpretation presents the possibility that a compound identified as a PIC was actually a compound (POHC) present in the waste that was not detectable (< 100 ppm). It must be remembered that the analysis of the stack samples will detect compounds present in the waste at ~ 100 ppm when achieving a destruction of 99.99%. Therefore, compounds present in the waste at < 100 ppm may also be detected in the stack samples if their DRE is less than 99.99%. Perhaps this fact does not conflict with the intent of the regulations, but in such cases the compound identified as a PIC will not actually be a "product" of incomplete combustion. Unfortunately, due to limitations imposed by detection levels in the waste, this problem cannot be avoided. Further explanation of the PICs selected from examination of the GC/MS data from the testing at the Cincinnati MSD incinerator is presented in the following paragraphs.

It seemed likely that PICs from the Cincinnati MSD wastes would be related to the halogenated compounds selected as POHCs. It also seemed likely that the potential PICs would be volatile rather than semivolatile compounds since incomplete combustion would probably result in smaller, rather than larger, molecules. Therefore, the data from the analyses of the volatile organic compounds in the stack gas bag and tank samples were checked first for the presence of candidate PICs. Several volatile halogenated compounds, such as chloroform and tetrachloroethylene, were immediately detected. Some additional halogenated compounds were detected which were familiar because of their routine detection in chlorinated drinking water. Also, the chemistry of these compounds indicates that they may be formed by free radical mechanisms under high temperature conditions. These compounds were bromodichloromethane (a POHC) and dibromochloromethane and tribromomethane (bromoform). The next step was to recheck for the presence of these latter two compounds in the waste feed samples. Waste feed Samples 7 through 9 did, of course, contain substantial amounts of bromodichloromethane (a selected POHC). However, dibromochloromethane and bromoform could not be detected in the waste feed samples. It thus appeared that dibromochloromethane and bromoform were PICs and that the source material, in waste feed Samples 7 through 9, was probably bromodichloromethane. However, since this compound was not found in waste feed Samples 1 through 6, another compound must have been responsible for the formation of the dibromochloromethane and the bromoform in Runs 1 through 6. Dibromoethane was later identified in the samples but at low concentration (~ 100 ppm).

After identifying the two possible PICs in the integrated gas samples, the GC/MS data from the MM5 trains were also examined. This examination did not reveal the presence of any compounds that should be selected as PICs, considering the relative concentration of dibromochloromethane and bromoform that were present in the integrated gas samples. Both of these are on the list of POHCs under the category Halomethane, N.O.S. Therefore, the two PICs selected for both wastes were tribromomethane (bromoform) and dibromochloromethane.

The emission rate for the above two PICs was calculated and then divided by the total input rate for the six POHCs selected in the waste feed. These calculations showed that the PIC emissions did not exceed 0.01% of the POHC input. These calculations meet our interpretation of EPA's proposed regulation on allowable emission levels of PICs, but the regulations might be circumvented. That is, the 0.01% limit was met in these tests only because some of the six POHCs selected were present at relatively high concentrations (1,000 to 10,000 ppm). From this, it is obvious that if at least one compound present in high concentration in the waste is selected as a POHC, it will be much more likely that the 0.01% limit will be met. Inclusion of a high concentration compound as one of the selected POHCs is not inconsistent with the regulations or the Guidance Manual, and would probably be encouraged. However, there should be an awareness that percentage emission of PICs is dependent on the concentration of the input POHCs selected.

HCl Removal Efficiency--

HCl removal efficiency of 99% is stipulated in the regulations published on January 23, 1981, but allows the removal efficiency to be determined based on Cl input in the waste and measurement of HCl out the stack. This means that scrubber inlet sampling is not required. For this reason, the test plan included Cl analysis of the waste and use of two Cl^- sampling trains operated on each test day. The sampling train used was that described in a draft of the Guidance Manual dated December 31, 1980. That train basically consists of a heated probe with a glass wool plug at the probe inlet (intended to remove particulate) followed by small midget impingers containing caustic solution (NaOH). Use of this train caused a serious problem with the results as is discussed below along with notation of a much more appropriate method recommended in the A. D. Little manual.

Calculated HCl removal efficiency results for the first waste (Runs 1 through 6) are given in Table 11. These results show that there were no tests in which a removal efficiency of 99% was achieved. However, the regulations require 99% HCl removal, whereas the stipulated sampling method measures total chloride emissions. Thus, if there is any mist or droplets of the scrubbing solution in the stack, they will probably be captured by the glass wool plug used in the front of the HCl sampling probe and probably also in other components of the train. For this reason, Table 11 also shows HCl removal when excluding the chloride determined in the plug component of the sampling train, which was quite large in all tests. To ascertain this, the plug rinse samples were later analyzed for sodium ion, and results showed that greater than 85 wt. % of the chloride was probably present as NaCl. Therefore, if one estimates chloride removal efficiency excluding the plug, then it can be seen from Table 11 that the 99% removal efficiency was achieved in 6 of 12 runs.

The above Cl^- analysis results were not received prior to the running of the second set of tests (Runs 7 through 9) so the same sampling train was used without any changes. In addition, the demister in the top of the absorber had failed before Runs 7 through 9. Apparently the lack of the demister increased carryover of droplets which had a serious impact on the HCl samples. Because these samples were very high in chloride, the impingers, as well as the plug, were analyzed for Na. These also showed high percentage Na, relative to the Cl^-, even in the impingers after correcting for the Na initially charged into the impingers as NaOH. For this reason, the results from the sampling train (midget impinger train) are not valid representations of HCl emissions, and were not used to calculate removal efficiency.

TABLE 11. SUMMARY OF CHLORIDE REMOVAL EFFICIENCY DATA FOR RUNS 1 THROUGH 6

Date	Run No.	HCl test No.	Cl in waste feed (%)	Chloride removal efficiency (%) Total	Chloride removal efficiency (%) Excluding plug
7/21/81	1	1A	2.91[a]	95.3	97.7
7/21/81	1	1B	2.91[a]	95.7	99.3
7/23/81	2	2A	8.22	98.9	99.8
7/23/81	2	2B	3.17	96.5	98.9
7/24/81	3	3A	7.08[a]	98.4	99.7
7/24/81	3	3B	7.08[a]	98.5	99.8
7/25/81	4	4A	4.05	96.6	99.2
7/25/81	4	4B	4.74	83.1	97.8
7/26/81	5	5A	5.88[a]	93.3	97.7
7/26/81	5	5B	5.88[a]	92.2	98.5
7/27/81	6	6A	6.97[a]	96.6	99.7
7/27/81	6	6B	6.97[a]	0	67.9

[a] The 6-hr integrated waste feed sample was the only sample analyzed for Cl. Other analyses shown are for the 2-hr waste feed samples.

About the time these calculations were being made, a copy of the A. D. Little manual was received. In reviewing that manual, it was noted that no mention was made of the midget impinger sampling train for HCl. Instead, the manual indicated that HCl sampling should be done by addition of a caustic impinger in the MM5 train used for POHC and particulate sampling.

The MM5 trains used in the testing at the Cincinnati MSD did not include a caustic impinger. But it was reasoned that the large volumes of condensate collected in the MM5 train would probably be quite effective in capturing HCl, as might the subsequent impingers (H_2O_2 and persulfate impingers). Based on this assumption, the condensate, H_2O_2, and persulfate impinger solutions were analyzed for Cl.

Cl^- analysis results for the individual impinger solutions showed that 92 to 99% of the Cl was present in the condensate in five of the six runs, with the remaining run showing 62%. For this one run, 35% was found in the H_2O_2 impinger. The persulfate impinger always contained the smallest percentage Cl , but it is an acid solution, so it may not effectively collect HCl.

Since the above data supported the expectation that the condensate (and H_2O_2 impinger) would be effective in collecting HCl, these Cl^- analysis results were used to estimate HCl removal efficiency. These results are presented in Table 12, but they can be considered only estimates since the train did not include a caustic impinger.

TABLE 12. ESTIMATED CHLORIDE REMOVAL EFFICIENCY FOR RUNS 7 THROUGH 9[a]

Date	Run No.	MM5 train No.	Cl in waste feed (%)	Chloride removal efficiency (%)
9/30/81	7	M5(2)-7A	13.0	99.8
	7	M5(2)-7B	13.5	99.2
10/1/81	8	M5(2)-8B	16.2	99.0
	8	M5(6)-8B	15.1	98.3
10/2/81	9	M5(2)-9A	15.9	95.6
	9	M5(2)-9B	15.9	94.9

[a] Results based on analysis of impinger solutions in MM5 trains, but which did not include a caustic impinger.

It is interesting to note in Table 12 that the Cl^- removal decreased in Run 9. Just prior to this run the plant's continuous pH monitor was found to be malfunctioning and the pH of the scrubbing solution was actually quite low (~ 1). Run 9 also represented the highest waste feed rate and highest stack gas flow rate.

As mentioned above, the A. D. Little manual recommends addition of a caustic impinger in the MM5 train and Cl^- analysis of the condensate and the caustic. A major advantage of this method is that any droplet carryover from a scrubber would probably be vaporized in the heated probe and heated filter box preceding the impinger. This should, therefore, give a much more accurate determination of HCl emissions, since any solids (e.g., NaCl) in the droplets should be removed by the filter.

Particulates--

Particulate concentration is limited, under the interim final regulation of January 23, 1981, to 180 mg/dscm (corrected to 12% CO_2). Accordingly, the test plan included measurement of the particulate emission as prescribed by EPA Method 5, but as a part of the POHC sampling train (Modified Method 5 train). This should in no way affect the particulate measurement since it merely meant that in some tests certain trains were analyzed for particulate weight prior to extraction of POHC's (as recommended in the A. D. Little manual).

Results of the particulate determinations are summarized in Table 13. This table shows the measured particulate concentrations and the particulate concentrations corrected to 12% CO_2 and to 7% O_2, shown below:

$$C_{corr} = \frac{(12\%)}{(\%\ CO_2)} (C_{actual})$$

$$C_{corr} = \frac{(14\%)}{(21 - \%\ O_2)} (C_{actual})$$

Where C_{corr} represents corrected particulate concentrations, % CO_2 and % O_2 are percentages in the stack gas, and C_{actual} is the measured particulate concentration.

The 12% CO_2 correction is the normal reporting procedure and the 7% O_2 correction is based on a request by the EPA project officer. As can be seen in Table 13, the particulate concentrations were much higher in Runs 7, 8, and 9, all three of which were well above the Resource Conservation and Recovery Act limit of 180 mg/dscm (corrected to 12% CO_2). However, it must be pointed out that during Runs 1 through 6, the sound dampeners in the stack were deteriorating, resulting in carryover of fiberglass particles. The sound dampeners were replaced prior to Runs 7, 8, and 9, but before these later runs, the mist eliminator had failed and was no longer in place. Therefore, the high particulate concentrations in these runs could be due to carryover of mist/droplets from the scrubber. In order to meet the required particulate level with a scrubber, it appears as though one must have a mist eliminator downstream of the scrubber, at least for this unit.

TABLE 13. SUMMARY OF PARTICULATE DETERMINATIONS

		Particulate concentration		
Date	Run No.	mg/dscm	mg/dscm corrected to 12% CO_2	mg/dscm corrected to 7% O_2
7/23/81	2	212	327	277
7/26/81	5	82	147	129
9/30/81	7	1,220	2,230	2,040
10/1/81	8	952	1,710	1,530
10/2/81	9	808	1,130	1,000

Emission of Vaporous Metals--

Emission of metals is not covered in the interim final regulations but is addressed in the proposed regulations. The Guidance Manual did not indicate that anything other than potentially vaporous metal emissions (i.e., Hg, As, Se) should be determined in a trial burn. These metals are determined by analysis of the special impinger included in the MM5 train. Therefore, this sampling and analysis was included in the test plan.

Results from the analysis of the special impingers for Runs 1 through 6 are shown in Table 14. In no case was the concentration of As above the detection limit. For Hg and Se, several values were above, but very close to, the detection limits. For Runs 7 through 9, it was discovered that the silver catalyzed ammonium persulfate solution used in the special impingers was improperly prepared. Therefore, even though the analysis was done, we have not reported these data. However, based on a comparison of the concentration of the vaporous metals (As, Se, Hg) in the waste in Runs 1 through 6 and those in Runs 7 through 9 (see Appendix E), it was observed that the concentration of these metals in Runs 7 through 9 was equal to or less than the concentration in Runs 1 through 6. It can, therefore, reasonably be assumed that the levels of these metals in the stack in Runs 7 through 9 would be comparable to, or less than, those observed in Runs 1 through 6.

Although not included in this test plan, the manual prepared by A. D. Little does indicate extraction and analysis of the particulate for metals, as well as analysis of the special impinger solution. But some question arises here as to why analysis for vaporous metals is not also necessary on the condensate or other impingers (caustic) that precede the special impinger. It would seem reasonable to expect that cooling of the gas stream could cause some of the vaporous metals (Hg, As, Se) to be collected in these impinger solutions. EPA has subsequently cleared up this question, stating that the condensate should also be analyzed for the vaporous metals.

TABLE 14. CONCENTRATION OF VAPOROUS METALS IN STACK EFFLUENT ($\mu g/m^3$) BASED ON ANALYSIS OF SPECIAL IMPINGER IN MM5 TRAINS FOR RUNS 1 THROUGH 6

Run No.	Train No.	As	Hg	Se
1	2 hr-A	< 5.4	< 0.26	< 3.5
	2 hr-B	< 0.1	< 0.1	< 0.6
	6 hr-A	< 0.24	< 0.65	< 0.58
	6 hr-B	< 1.1	< 0.1	< 0.94
2	2 hr-A	< 6.6	0.3	< 2.1
	2 hr-B	< 0.9	< 0.2	< 2.8
	6 hr-A	< 0.1	< 0.08	< 0.89
	6 hr-B	< 0.09	< 0.05	< 0.59
3	2 hr-A	< 3.1	< 0.3	< 4.0
	2 hr-B	< 0.6	0.6	< 2.0
	6 hr-A	< 1.0	0.1	< 1.2
	6 hr-B	< 1.8	< 0.1	< 1.2
4	2 hr-A	< 2.5	< 0.2	< 5.9
	2 hr-B	< 0.60	0.2	< 5.2
	6 hr-A	< 0.39	0.23	< 0.19
	6 hr-B	< 0.2	< 0.01	< 1.8
5	2 hr-A	< 0.72	< 0.3	< 4.7
	2 hr-B	< 0.69	< 0.3	< 4.6
	6 hr-A	< 0.22	< 0.1	< 1
	6 hr-B	< 0.20	< 0.09	< 1.3
6	2 hr-A	< 4.0	< 0.2	< 5.3
	2 hr-B	< 3.4	0.3	< 4.5
	6 hr-A	< 1.1	< 0.2	< 2.1
	6 hr-B	< 0.58	< 0.1	< 2

Other Gaseous Emissions--

In developing the test plan based on the protocol in the Guidance Manual, it was necessary to include other gaseous emissions. The plan, therefore, included continuous monitoring of the stack effluent for O_2, CO, NO_x, and HC throughout each test.

The range and average value for each of the gaseous effluents during each test period are shown in Table 15. Referring back to the test matrix in Table 6, these data clearly show the decrease in O_2 with increasing temperature. There are no obvious correlations of CO, NO_x, or HC with temperature, residence time, or type of waste.

Bottom Ash and Scrubber Effluent

Composite samples of bottom ash and scrubber effluent were taken on each test day. This process consisted of compositing the three grab samples of scrubber effluent and compositing the four grab samples of bottom ash sluiced out of the unit. Each of these samples was analyzed for the six selected POHCs in accordance with the Guidance Manual. However, such data are not required in computing DRE, and the existing regulations do not require such analysis for comparison with any limitation in the regulations. Thus, even though it is unclear why they should be analyzed for POHCs, the specified sampling and analysis were carried out.

Results of the analysis, by both MRI and Rockwell, are given in Table 16A (Runs 1 through 6) and Table 16B (Runs 7 through 9). None of the POHCs was present in concentrations above the detection limits in scrubber effluent samples. Bottom ash samples did contain detectable levels of volatile POHCs, which decreased with increasing temperature in the combustion chamber, with the exception of Run 6 (at the highest temperature). Results from both MRI and Rockwell showed much higher concentrations of the three volatile POHCs in Run 6. At present, we know of no good explanation for this finding.

QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES AND DATA

QA/QC was an integral part of this project, with emphasis on the analysis of POHCs in the waste feed. These procedures included field audits and laboratory audits by MRI's internal Quality Assurance Section, and a report on the results of that QA audit phase of this project is attached as Appendix I.

As a part of those laboratory audits, samples were prepared synthetically by the QA Section and submitted as blind samples to the analytical groups at MRI and Rockwell for analysis. The results of this interlaboratory audit showed that MRI's relative accuracy was within ± 30% of the theoretical (known) value for most of the constituents, but was as high as + 138% in two cases and + 213% in one case. Rockwell's accuracy was about the same; its results ranged from - 28% to + 57% for most of the constituents but was as high as + 159% in one case. The maximum difference between MRI and Rockwell, based on the relative accuracy for each reported constituent, was 76%. The relative accuracy of MRI and Rockwell agreed 79% of the time at the ± 25% acceptance level.

TABLE 15. SUMMARY OF DATA FROM CONTINUOUS GAS MONITORS

Date	Run No.		Oxygen (%)	Carbon monoxide (ppm)	Nitrogen oxides (ppm)	Hydrocarbons[a] (ppm)
7/21/81	1	Range	10.9-13.7	0-1.8	84-140	0.5-10.4
		Avg.	12.2	0.6	122	2.1
7/23/81	2	Range	7.5-12.0	0-56	131-163	0-9.6
		Avg.	10.3	3.6	146	3.3
7/24/81	3	Range	6.3-14.7	0-17.5	64-182	0-9.4
		Avg.	7.8	8.2	118	1.8
7/25/81	4	Range	11.7-14.2	0-42.2	98-160	0.7-3.0
		Avg.	13.0	16.8	137	1.1
7/26/81	5	Range	8.6-11.6	1.9-11.6	82-239	0-2.8
		Avg.	10.5	7.0	136	0.7
7/27/81	6	Range	6.2-10.4	0-5.6	95-172	0.3-2.3
		Avg.	8.4	3.0	135	1.3
9/30/81	7	Range	11.0-13.0	0-20.4	113-151	0-2.0
		Avg.	12.3	3.3	132	0.5
10/1/81	8	Range	10.0-11.5	5.4-13.6	140-152	0.5-3.0
		Avg.	10.6	8.9	145	1.7
10/2/81	9	Range	8.3-9.8	6.6-15.8	123-134	0.2-1.5
		Avg.	9.1	10.6	130	0.6

[a] ppm (wet); calibrated against propane.

TABLE 16A. RESULTS OF ANALYSIS OF SCRUBBER EFFLUENT AND BOTTOM ASH SAMPLES FOR POHCs (RUNS 1 THROUGH 6)

	Scrubber effluent (μg/L)[a]					
POHC	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Chloroform	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)
Carbon tetrachloride	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)
Tetrachloroethylene	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)
Hexachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Hexachlorobenzene	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
HCCP[b]	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)
	Bottom ash (μg/L[a])					
	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Chloroform	4 (115)	< 1 (< 5)	< 1 (< 5)	4 (6)	2 (3)	440 (550)
Carbon tetrachloride	6 (25)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)	< 1 (< 5)
Tetrachloroethylene	4 (35)	< 1 (< 5)	< 1 (< 5)	2 (2)	1 (1)	40 (45)
Hexachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Hexachlorobenzene	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
HCCP	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)

[a] Numbers in parentheses are values reported by Rockwell.

[b] Hexachlorocyclopentadiene.

TABLE 16B. RESULTS OF ANALYSIS OF SCRUBBER EFFLUENT AND BOTTOM ASH SAMPLES FOR POHCs (RUNS 7 THROUGH 9)

POHC	Scrubber effluent (μg/L)[d]		
	Run 7	Run 8	Run 9
Trichloroethane[a]	< 2 (< 5)	< 2 (< 5)	< 2 (< 5)
Tetrachloroethane[b]	< 2 (< 5)	< 2 (< 5)	< 2 (< 5)
Bromodichloromethane	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)
Pentachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Hexachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Dichlorobenzene[c]	< 7.5 (< 15)	< 7.5 (< 15)	< 7.5 (< 15)
	Bottom Ash (μg/L)		
	Run 7	Run 8	Run 9
Trichloroethane	2 (< 5)	< 2 (< 5)	< 2 (< 5)
Tetrachloroethane	2 (< 5)	< 2 (< 5)	< 2 (< 5)
Bromodichloromethane	< 5 (< 5)	< 5 (< 5)	< 5 (< 5)
Pentachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Hexachloroethane	< 2.5 (< 5)	< 2.5 (< 5)	< 2.5 (< 5)
Dichlorobenzene[c]	< 7.5 (< 15)	< 7.5 (< 15)	< 7.5 (< 15)

[a] Combined concentrations of 1,1,1-trichloroethane and 1,1,2-trichloroethane.

[b] Combined concentrations of 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane.

[c] Combined concentrations of 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene.

[d] Numbers in parentheses are values reported by Rockwell.

All constituents in these samples were at low concentrations, ranging from 13 to 109 μg/ml, but the samples were quite "clean" since they were synthetically prepared samples. Relative precision on the audit samples was very good, for both MRI and Rockwell, with the highest (worst) relative precision for MRI of ± 27% and ± 8% for Rockwell.

The major point here is that the comparisons of relative precision and relative accuracy between the MRI and Rockwell audit samples do not seem entirely consistent with the results reported by the two laboratories for the actual waste feed samples. As pointed out in the memo in Appendix I, such disagreement is most probably caused by matrix effects or differences in the samples. Therefore, the following paragraph presents a discussion of the QA/QC procedures and results for the actual waste feed samples. More details on all of the QA/QC work done by MRI are attached in Appendix J.

Analysis of waste feed samples by MRI and Rockwell was done using identical analytical procedures, including quantification against authentic standards. Therefore when intra- and interlaboratory variations are evaluated, the QA/QC results provide the best source of information, which is the reason that QA/QC procedures were an integral part of this project. Such procedures included spiking of some samples with the compounds (POHCs) of interest (i.e., fortifications) and/or spiking with surrogate compounds, to determine percent recovery, and duplicate or triplicate analysis of some of these samples. Duplicate analysis provides a good indication of the precision of the results, while spiking provides an indication of the accuracy.

MRI performed duplicate analysis on fortifications of three of the waste feed samples. That is, for these three samples, two (or three) separate aliquots were taken from each sample and each was fortified identically with the subject POHCs, which were then analyzed. These analytical results thus provide information on both the precision and the accuracy (percent recovery) of the work performed.

Table 17 shows the MRI results for each of the replicate analyses of the fortified samples in terms of the final concentration determined from the analysis. As can be seen, the relative standard deviations (RSD) for the replicate analyses of each POHC show good precision, and all are well within the limit of 30% stipulated in the A. D. Little manual. It could, of course, be argued that precision on fortified samples (i.e., higher concentration levels) might be better than the precision at the lower concentrations in the actual samples, since the fortifications were generally 2 to 5 times the measured concentration. However, as presented in Appendix J, these same replicates were also analyzed for some of the other compounds that were present, but for which no fortifications were made, and those results support the conclusion that MRI's analytical precision was good. Rockwell did not report any results on replicate POHC analyses of any sample, but as discussed below, their replicate analysis of surrogates indicates that their precision was also good, with the possible exception of chrysene-d12. Thus, the next step was to evaluate QA/QC data on spiking or fortifications (i.e., percent recovery), which provides a measure of the accuracy of the analyses.

TABLE 17. REPLICATE ANALYSIS RESULTS FOR FORTIFIED WASTE FEED SAMPLES[a] (g/g)

	Run 2 - replicates		RSD	Run 5 - replicates			RSD
	S1	S2	(%)	S1	S2	S3	(%)
Chloroform	21,000	17,000	15	57,000	59,000	58,000	2
Carbon tetrachloride	12,000	10,000	13	21,000	23,000	21,000	5
Tetrachloroethylene	11,000	9,400	11	9,300	9,700	9,700	2
Hexachloroethane	NA	NA	-	1,600	1,700	1,800	6
Hexachlorobenzene	NA	NA	-	NA	NA	NA	-
HCCP	31,000	34,000	7	31,000	37,000	33,000	9

	Run 8 - replicates		RSD
	S1	S2	(%)
1,1,2-Trichloroethane	21,000	19,000	7
1,1,1,2-Tetrachloroethane	13,000	12,000	6
1,1,2,2-Tetrachloroethane	13,000	13,000	0
Bromodichloromethane	NA	NA	-
Pentachloroethane	24,000	20,900	10
Hexachloroethane	6,900	5,800	12
1,2-Dichlorobenzene	3,900	3,400	10

[a] 6 hr integrated samples.

NA - Not analyzed in duplicate, for the same level of fortification.

MRI spiked (fortified) three waste feed samples with the subject POHCs at a level generally 2 to 5 times the detected concentration, or at 10 times the detection limit when the detected concentration was below the detection limit. Rockwell used a somewhat different, but certainly valid, technique of spiking all samples with three or five surrogates.* Both laboratories were thus able to determine a percent recovery for the compound(s) spiked into the samples.

Results reported by Rockwell on recovery of the surrogates spiked into each waste feed sample are shown in Table 18. As can be seen in Table 18, the recovery of surrogates reported by Rockwell was quite good, with the possible exception of one of the semivolatile surrogates (chrysene-d12).

TABLE 18. RECOVERY OF SURROGATES DETERMINED BY ROCKWELL FOR SPIKED WASTE FEED SAMPLES

Surrogate	Samples from Runs 1-6 Mean (%)	Samples from Runs 1-6 % RSD	Samples from Runs 7-9 Mean (%)	Samples from Runs 7-9 % RSD
Bromochloromethane	103	6	102	5
Benzene-d6	101	6	97	5
Toluene-d8	102	6	94	4
p-Bromofluorobenzene	102	4	96	5
Naphthalene	117	32	140	11
Chrysene-d12	118	78	160	56
DFTPP	93	16	89	9

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* Surrogates used by Rockwell were:

Semivolatiles	Volatiles
Naphthalene-d8 (100 μg/g level)	Bromochloromethane
Chrysene-d12 (100 μg/g level)	Benzene-d6
DFTPP (1,000 μg/g level)	Toluene-d8
	1,4-Dichlorobutane
	p-bromofluorobenzene

Note: spike level for each of the above five volatiles was 20 μg/liter in the final dilution.

Recoveries of the actual POHCs from three fortified waste feed samples, as determined by MRI, are shown in Table 19. These also show good recoveries, with the exception of the high recoveries of two semivolatile POHCs in the sample from Run 8 (pentachloroethane and 1,2,-dichlorobenzene). Thus, both the Rockwell and MRI data seem to show recovery efficiencies considerably greater than 100% for some semivolatile compounds in the waste feed samples from Runs 7 to 9.

The high recoveries found by MRI for pentachloroethane and 1,2-dichlorobenzene, in the sample from Run 8, would probably indicate that the actual concentrations of those POHCs in the samples were higher than the reported values. Supporting this is the fact that the concentrations of the three semivolatile POHCs in waste feed samples from Runs 7 to 9, as reported by Rockwell, were higher in most cases than those reported by MRI. If Rockwell values are more nearly correct, the effect would be to raise the DRE values.

In regard to the analysis by both laboratories, to the best of our knowledge, the values were determined for the same waste sample. The waste feed samples were split by MRI and sent to Rockwell for analysis. Every effort was made to mix samples thoroughly before they were split, and both laboratories used the same procedures in taking aliquots from those samples for analysis. However, there always remains the possibility that the samples might be different. This would seem to be a greater potential problem for the samples from Runs 1 through 6, since they were multiphasic with high water content.

In summary, the data discussed above for the waste feed samples show that:

- Analytical precision of both laboratories was good.
- Analytical accuracy of both laboratories, based on recovery data, was good, with the probable exception of the three semivolatile POHCs in Runs 7 through 9.

Another important aspect of the QA/QC procedures pertains to accuracy and precision of the stack effluent samples. This area is also discussed in Appendix J. Information in that appendix shows good precision, but somewhat lower than expected recovery efficiency, for the MM5 condensate samples. It also shows the need to develop methods for determining recovery efficiency on solid substrates (i.e., the filter and XAD resin). However, all this information on precision and recovery efficiency had limited utility, since most of the reported values for POHCs in the MM5 train samples were below the detection limits.

TABLE 19. RECOVERIES OF POHCs DETERMINED BY MRI FOR FORTIFIED WASTE FEED SAMPLES (%)

POHC	Run 2		Run 5			Mean	RSD (%)
	S1	S2	S1	S2	S3		
Chloroform	130	97	90	95	93	101	16
Carbon tetrachloride	100	81	78	89	78	85	11
Tetrachloroethylene	97	77	82	86	85	85	9
Hexachloroethane	121	183	109	102	98	123	28
Hexachlorobenzene	-	112	146	148	-	135	15
HCCP	113	117	109	134	120	119	8

	Run 8		Mean	RSD (%)
	S1	S2		
1,1,1-Trichloroethane	130	-	-	-
1,1,2-Trichloroethane	110	110	110	0
1,1,1,2-Tetrachloroethane	100	95	97	4
1,1,2,2-Tetrachloroethane	110	110	110	0
Bromodichloromethane	NA	NA	-	-
Pentachloroethane	211	178	195	8
Hexachloroethane	NA	NA	-	-
1,2-Dichlorobenzene	226	192	209	8

NA - Not analyzed (no fortifications made for this POHC).

SECTION 8

EVALUATION OF INCINERATOR PERFORMANCE AND ENVIRONMENTAL ASSESSMENT

A tabulation of data on the incinerator performance and effluents, as determined in each of the tests, is given in Table 20. All these data have been presented earlier in various sections of the report and are abbreviated in the table.

In evaluating the data in Table 20, the reader is reminded that Runs 1 through 3 were those with the forced draft fan dampers closed to yield the highest residence time possible, which was the normal mode of operation at the time but was not up to the design of the unit. Runs 4 through 6 and 7 through 9 were done with the fan dampers 50% open, giving a lower residence time and requiring a higher waste feed rate to achieve the desired temperature.

INCINERATOR PERFORMANCE

Generally, the incinerator performed well, especially in Runs 7 through 9. In Runs 1 through 6, a loose electrical connection caused several "trip-outs," but this was corrected. No burner plugging or waste feed problems occurred that might have affected performance during the testing. The unit operated quite well in automatically adjusting the waste feed rate to maintain the set point temperature. It was obvious from temperature-time readings that changes were occurring in the heating value of the waste being fed. Temperature swings of 56 to 111°C (100 to 200°F) occurred in the kiln, cyclone furnace, and combustion chamber before the unit could be "lined out" again by the operators or by the automatic controls. Usually, the temperature excursions were not severe enough or of long enough duration to warrant interrupting a test.

Overall performance of the incinerator and combustion system was good, but there were some problems with the scrubber. Previous experiences of the plant had shown that solid material tended to build up on the sieve trays, plugging the holes and restricting flow through the unit. Just prior to Run 7, the incinerator had to be shut down to open up the scrubber and use high pressure water hoses to remove the solids buildup from the sieve trays. Even after that, in Runs 7 through 9, the high flow rate with the fan dampers 50% open showed that the unit was just able to maintain the desired negative pressure in the combustion chamber.

TABLE 20. TABULATION OF INCINERATOR PERFORMANCE DATA

Run No. Date	Pesticide-containing waste							High chlorine waste		
	1 7/21/81	2 7/23/81	3 7/24/81	4 7/25/81	5 7/26/81	6 7/27/81		7 9/30/81	8 10/1/81	9 10/2/81
Waste feed rate (kg/min)	32.7	34.0	38.1	53.1	53.5	60.3		49.0	61.2	62.1
Chamber temperature (°C)	899	1093	1316	899	1093	1316		899	1093	1316
Residence time (sec)	3.3	3.7	3.4	2.2	1.8	1.7		2.3	2.0	1.5
Stack gas flow rate (dscm)	696	526	490	1020	1080	1010		976	1000	1160
O_2 Conc. in stack gas (%)	12.2	10.3	7.8	13.0	10.5	8.4		12.3	10.6	9.1
DRE for POHCs (%):[a]										
Chloroform	99.99	N/A	99.99	99.99	99.99	99.99	Trichloroethane	99.99	N/A	99.99
Carbon tetrachloride	99.99	N/A	99.99	99.99	> 99.96	> 99.9[d]	Tetrachloroethane	99.99	N/A	99.99
Tetrachloroethylene	99.99	N/A	99.99	99.99	99.99	> 99.97	Bromodichloromethane	99.97	N/A	99.99
Hexachloroethane	99.99	99.99	99.99	99.99	99.99	99.99	Pentachloroethane	99.99	99.99	99.99
Hexachlorobenzene	99.99	99.99	99.99	99.99	99.99	99.99	Hexachloroethane	99.99	99.99	99.99
Hexachlorocyclopentadiene	99.99	99.99	99.99	> 99.96	99.99	> 99.97	Dichlorobenzene	99.99	99.99	99.99
HCl removal effiency (%)[b]	98.5	99.4	99.7	98.5	98.1	83.8		99.5	98.7	95.3
Particulate Conc. (mg/dscm)[c]	N/A	327	N/A	N/A	146	N/A		2,230	1,710	1,130
Conc. of other pollutants										
CO (ppm)	0.6	3.6	8.2	16.8	7.0	3.0		3.3	8.9	10.6
NO_x (ppm)	122	146	118	137	136	135		132	145	130
HC (ppm)	2.1	3.3	1.8	1.1	0.7	1.3		0.5	1.7	0.6
Maximum Conc. of POHCs (µg/L):										
Scrubber effluent	< 5	< 5	< 5	< 5	< 5	< 5		< 7.5	< 7.5	< 7.5
Bottom ash	< 5	< 5	< 5	< 5	< 5	440		< 7.5	< 7.5	< 7.5

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[a] DRE values are shown only to two decimal places, using 99.99 even if calculated value was >99.99. Only the lowest value is shown.

[b] HCl based on excluding analysis of plug rinse. For Runs 7-9, values are estimates based on Cl analysis of MM5 trains.

[c] Particulate conc. adjusted to 12% CO_2.

[d] Due to low waste feed concentration and inadequate stack gas sample volume, DRE could not be calculated to more than one decimal place.

When the scrubber was opened up to clean the sieve trays, it was found that the vane-type demister had failed and fallen onto the top tray. It was removed but no replacement was available. Initial operations after startup did not show any discharge of liquid from the induced draft fan suction drains so it was assumed that operation without the demister had not caused any significant carryover of liquid. As discussed in Section 7, the particulate test results indicate that the lack of a demister may have caused the highly particulate concentrations found for Runs 7, 8, and 9.

The plant problems with buildup of solids on the sieve trays were found to be worse if the scrubber was operated at pH above 6. Therefore, the plant generally tried to operate without exceeding a pH of 6.0.

The plant is equipped with a continuous pH monitor which controls makeup of caustic to the scrubber. Unfortunately, the unit malfunctioned sometime during the last series of tests (apparently after Run 7). As a result, the pH of the scrubbing solution was quite low (~ 1.0) during at least part of Run 9. This was probably the reason for the lower HCl removal efficiency measured for Run 9. Scrubber water samples should be checked with pH paper during a trial burn to avoid such problems.

This test program necessitated achieving the desired test conditions prior to each test. Achieving the desired temperature took a little time but was no problem. Achieving the desired residence time was slightly different. That is, the residence time is mainly determined by the openings on the FD fans and, to a lesser extent, by the combustion chamber temperature. The fan opening (e.g., 50%) refers only to the damper position (not the flow rate) and there were no air flow meters. Thus, the only way to estimate residence time for any fan opening was to do a velocity traverse of the stack with the MM5 equipment. The 50% fan setting was selected when the stack velocity traverse data indicated about double the flow of that when the dampers were closed.

One very important aspect of the incinerator trial burn, was the quantity of waste required. In Runs 7 through 9 the waste feed rate was about 61 kg/min (135 lb/min), equivalent roughly to 75,000 liters/day (20,000 gal/day) or about four tank truck loads. If waste had continued to be burned at that rate over 3 test days, it would have required 227,000 liters (60,000 gal.), which is a significant percentage of the total storage capacity. Also, there must be enough waste to provide an adequate margin of safety and allow for the fact that a tank cannot be pumped out below a certain level (i.e., the available quantity is less than what is stored in the tank). As a result, if a trial burn is to use the same waste for 3 test days, the quantity of waste feed required may be quite large relative to the available storage capacity. Also, as discussed earlier, it may be difficult to know the composition of the waste to be burned unless the entire volume required can be held in storage over the period necessary for analysis of samples and activating a test crew. Of course, it could be a major problem in some cases, if the waste feed has to be held for approval of the trial burn permit which include those analysis results.

ENVIRONMENTAL ASSESSMENT OF INCINERATOR PERFORMANCE

DRE values were obtained for each of the six POHCs selected in the two wastes tested in this program, as shown in Table 20 and in Appendix H. Almost all DRE values were 99.99% or above, although, in a few cases, analysis problems made it necessary to report results that do not clearly show 99.99% (e.g., > 99.9%). There was only one test where it was clear that 99.99% was not achieved. This occurred in Run 7, at 899°C (1650°F), wherein the DRE of bromodichloromethane was determined to be 99.97%. No DRE could be determined for the next test at 1093°C (2000°F) during Run 8, but at 1316°C (2400°F) for Run 9, the DRE for this compound was 99.995%. It can, therefore, be concluded that 899°C (1650°F) is too low to destroy 99.99% of the compound, but that the higher temperature is sufficient.

Data on bromodichloromethane provided the only instance in which temperature could be seen to have an effect on DRE. For all other POHCs, it would have to be concluded that a temperature of 899°C (1650°F) is sufficient for 99.99% DRE, at least at the residence times of these tests. None of the test data show much, if any, effect of residence time on DRE, but even the lowest residence time of 1.5 sec is still relatively long compared to that of some other incinerators designed for 0.5 sec residence time or less.

When the EPA published the incinerator regulations on January 23, 1981, the preamble to those regulations stated that an initial analysis of available data indicated that most organic wastes will present no significant health hazards when treated to a 99.99% DRE. On this basis, the data obtained in the trial burns at the Cincinnati Metropolitan Sewer District incinerator make it reasonable to conclude that the incinerator presents no significant health hazard from the standpoint of organic emissions. Presumably, the same can be said for the products of incomplete combustion, which did not exceed 0.01% of the input POHCs, as discussed in a previous section.

Under the Resource Conservation and Recovery Act regulations, there is no required combustion efficiency as computed from the concentrations of CO and CO_2 in the stack effluent, but regulations on incineration of PCB do require a combustion efficiency of at least 99.9%. Using this criterion, the tests at the Cincinnati MSD were always above 99.9%, with the lowest value being 99.95%.

RCRA regulations, which do address fugitive emissions, require that the combustion chamber be maintained at lower than atmospheric pressure, which was being done at the MSD incinerator. Daily inspection for leaks and spills, etc., is also required. During the trial burn, the only notation in this regard was some leakage of scrubber effluent in the operating area, but as noted in Table 20, no POHCs were ever detected in scrubber effluent.

The second major RCRA regulation for hazardous waste incinerators requires at least 99% HCl removal efficiency for wastes containing more than 0.5% Cl. Problems with the sampling procedure specified in the Guidance Manual for determining HCl emission make uncertain conclusions about the test results. However, for Runs 8 and 9, it can certainly be concluded that 99% removal efficiency was not achieved. As noted earlier, the lower HCl removal efficiency of 95.3% measured in Run 9 was probably caused by the low pH of the scrubbing solution that occurred after the pH monitor had malfunctioned. Since no further testing was conducted after Run 9, additional testing would be needed to check the HCl removal efficiency when the pH is under control and when using the sampling method specified in the A. D. Little manual.

The third major RCRA regulation limits the particulate concentration to 180 mg/dscm (corrected to 12% CO_2). This limit was met only in Run 5. Very high particulate concentrations were found in Runs 7, 8, and 9. It does seem likely that the high particulate concentrations were caused by an increased carryover of droplets of scrubbing solution after removal of the demister. This will not be known unless the unit is retested after replacement of the demister.

One interesting aspect of the results was that the 99.99% DRE was achieved, in spite of the high particulate concentration. This seems to confirm the fact that POHCs were all below the detection limit in the scrubbed stack gas and indicates that combustion may account for the high DRE rather than scrubbing being any significant part of the DRE.

Continuous monitoring data for CO, HC, and NO_x were obtained from the stack effluent. All the CO and HC concentration measurements obtained were quite low, as shown in Table 20. Average NO_x concentrations for each run were in the range of 118 to 146 ppm, comparing very favorably with NO_x emissions from power plants.

Analyses of POHCs in the scrubber effluent and the bottom ash sluiced from the kiln and combustion chamber were included in this project. All results were below detection limits except for a high value in the bottom ash sample in Run 6. The reason for the high value is unknown and seems inconsistent with the fact that only volatile POHCs were above detection limits, and Run 6 was at the highest temperature of 1316°C (2400°F).

In summary, the results of these trial burns to determine incinerator performance and conduct an environmental assessment showed that the unit operates quite well and can achieve the 99.99% DRE with a minimum of any other emission or effluent concerns with two exceptions, as follows:

1. High particulate concentrations indicate that the demister should be replaced as soon as possible.
2. Additional testing, using the recommended sampling method, needs to be done to ascertain that 99% HCl removal is achieved when the scrubber recirculating fluid is at the proper pH.

SECTION 9

EVALUATION OF TRIAL BURN PROTOCOL AND SUGGESTED REVISIONS

The experience and data acquired during this program form the basis for an evaluation of the regulatory procedures and trial burn protocol presented in this section. While it is believed that the specific comments contained in the following paragraphs have general applicability, the reader is reminded that these comments are based only on the work done at the Cincinnati Metropolitan Sewer District incinerator.

Interim final regulations published on January 23, 1981, limit emissions from hazardous waste incinerators as follows:

- ≧ 99.99% DRE
- ≧ 99% HCl removal
- ≦ 180 mg/dscm particulate concentration

Results from the testing carried out at the Cincinnati MSD incinerator show that the destruction and removal efficiency was achieved for the selected principal organic hazardous components. Although in several cases the HCl and particulate requirements were not met, the data do not give reason to believe that the above criteria cannot be achieved. However, certain aspects of the regulations pertaining to trial burns and the Guidance Manual can or did present problems. Evaluation of the protocol established in the regulations and in the Guidance Manual was the main purpose of this project. These evaluations are presented in three parts:

- Regulatory Procedures and Performance Parameters
- Sampling and Analysis Methods
- Economics of Trial Burns

REGULATORY PROCEDURES AND PERFORMANCE PARAMETERS

This program identified several factors that relate to implementation or interpretation of the interim final and proposed regulations and the protocol in associated documents (e.g., Guidance Manual). These factors are discussed in the following paragraphs, and MRI suggests that EPA carefully consider them as suggestions for possible revision or clarification of the regulations and associated documents.

Variability of Wastes

It must be realized that many commercial incinerators receive a wide variety of waste that will be intermixed with other wastes, stored in limited capacity facilities, and fed to the incinerator within a few days. As noted in the regulations published in the Federal Register of January 23, 1981 (pg. 7681), truck manifests will seldom adequately describe composition of the delivered waste, especially POHCs. As a result, there is no way for an incinerator operator to know if that waste is "significantly different" from any other, at least in POHCs. At best, the operator may know that it contains a high concentration of one or more POHCs, but the operator cannot be sure that it does not contain lower concentrations of other POHCs which may be much more difficult to destroy than the ones that are known. The operator, and EPA, must therefore say that those POHCs are "not reasonably expected to be present." In reality, the only thing that could be done is to require that the operator not burn wastes that are known to contain POHCs which are not included in his permit. Even then, the concentration of the POHCs is likely to be "significantly different" from any used in a trial burn on which his permit may have been based. There would, therefore, be some justification for allowing the operator to burn any waste containing any (known) POHCs that are less difficult to incinerate than the one on his list of permitted wastes that is more difficult to incinerate.

Alternatively, a design/operating practices regulation might be considered. For this approach to be viable, EPA would need to obtain data on the DRE for the POHCs that actually are the most difficult to destroy and establish the minimum temperature and residence time required for 99.99% DRE. In this regard, the POHCs selected in the Cincinnati tests are considered to be among those that are most difficult to destroy; yet, even at the lowest temperature of 899°C (1650°F), there was only one of those POHCs for which a DRE of 99.99% was not achieved. Thus, a design/operating practices regulation might not be unduly severe.

Storage of Waste

An operator may want to submit a trial burn application in order to get started, or to expand the list of compounds for which a permit already has been received. In that case, the regulations present one major problem. That is, under the regulation, the waste to be burned would have to be held in storage once it has been sampled for analysis. Unless this is done, it is very possible that the waste available at the time of the trial burn will be very different from the analysis submitted in the application.

As was pointed out elsewhere in this report, the relative amount of storage capacity to hold the waste may well be a large percentage of the plants total storage capacity. This storage volume would be tied up for however long it takes to analyze the samples, submit the data with the application, and await response from the permit reviewer. This might not be necessary for an incinerator that burns a limited number of wastes from very specific sources but could be a serious problem for a commercial facility receiving a wide variety of wastes.

The storage problem could be avoided if it were possible to hold a relatively small quantity of waste containing high concentrations of a POHC that is difficult to incinerate so that it could be burned with whatever other waste was available at the time of the trial burn, or even with just the auxiliary fuel.

POHC Selection Criteria

The POHCs to be selected are required to be "one or more," according to the regulations. The regulations are thus not specific and a permit reviewer could expand the number selected if it were so desired. On the other hand, POHCs selected on the basis of incinerability and concentration will be dominated by those that are difficult to incinerate, even if present only at 100 ppm. It would, apparently, be permissible to select one or more POHCs on this basis, plus other additional POHCs that are present in high concentration. But, if this is allowable, it will be much more likely that the PIC emission limit will be met. Thus, some clarification of the POHC selection criteria is needed.

PIC Identification and Selection

Identification of PICs is required under the interim final regulations, and their emission is limited under the proposed regulation. As noted therein, the PICs are difficult to predict and may, therefore, be selected from careful analysis of the gas chromatographic/mass spectrometric data for stack effluent samples taken in the trial burn. Thus, the number of PICs is not specified, as it probably cannot be. It is, therefore, suggested that PICs be identified and selected based on an evaluation of GC/MS data, rather than allowing one to attempt to predict PICs for complex waste mixtures. Also, as mentioned earlier, the PICs identified in the Cincinnati tests were assumed to be limited to compounds on the list of POHCs, but which were not detected in the original waste (< 100 ppm). If this assumption is correct, it needs to be stated in the regulation and/or the Guidance Manual. To do otherwise could greatly expand the sampling and analysis requirements and could, in effect, limit emission of all compounds that are not listed POHCs.

HCl Removal Efficiency

Under the regulations, an HCl removal efficiency of ≧ 99% is required. The Guidance Manual allows this efficiency to be calculated from the HCl output and the organic chlorine content of the input waste. A potential problem, therefore, exists if the waste contains a significant quantity of inorganic chlorine. However, the method stipulated for analysis of organically bound chlorine in the waste is a combustion method, which would be affected by inorganic clorine. It is, therefore, probably appropriate to base the determination of HCl removal on the results of this analysis method. Thus, the problem appears to be merely one of nomenclature.

Monitoring Requirements

Certain parts of the regulation that relate to monitoring seem to be of limited use, namely monitoring of air feed rate and hourly monitoring of plume color and opacity. Air feed rate is not monitored at many facilities, and in fact is rather difficult and expensive to do. More importantly, the apparent intent of the regulation would be better served by requiring continuous O_2 monitoring of the stack effluent (as well as CO). Also, hourly observations of plume color and opacity might be of some use to an operator but are rather difficult to do at the outlet of a wet scrubber (or at night) and should probably be deleted from the regulations.

SAMPLING AND ANALYSIS METHODS

Most of the evaluation work in the trial burn was concentrated on the sampling and analysis protocol given in the Guidance Manual[1] and related documents, specifically SW-846[3] and the A. D. Little manual.[2] Sampling and analysis are discussed separately below, although they are closely related.

Sampling

Sampling methods for streams such as liquid waste feed, scrubber effluent, and bottom ash, etc., are adequately described in the Guidance Manual. However, the protocol gives little or no information as to how often or how many such samples need to be taken during each test period. This information is most critical for the waste feed samples. Clearly, the most representative samples possible should be obtained. Consequently, it is recommended that, wherever possible, an integrated sample be taken, consisting of subsamples taken at 15-min intervals. This recommendation applies mainly to liquid wastes, but may not be necessary if the waste feed is known to be homogeneous and of consistent composition. Grab samples of scrubber effluent and bottom ash should be adequate, but the rationale for analyzing their POHC content is unclear since they are hazardous by definition and there is no guidance provided for evaluating the results.

Stack sampling was the most complex part of the actual field work and the protocol at that time was very limited, especially with regard to the specifics about the sampling train and the sampling time necessary. Much more detail on the MM5 train is now available in the A. D. Little manual,[2] but is considerably different than what is presented in the Guidance Manual,[1] so the latter needs to be revised. However, there were certain problems with the protocol, which are discussed below.

After consideration of the expected concentrations and the limits of chemical analysis, it was decided to use both 2- and 6-hr samples taken by MM5. Comparison of the data from 2- and 6-hr samples did not show any cases where it was clear that sampling for 2 hr was insufficient to ascertain whether 99.99% DRE was or was not achieved (relative to the detection limit of 1 μg). One possible exception to this was the DRE for hexachlorocyclopentadiene determined in Runs 4 and 6. The major problem in these cases was that the analysis of the waste feed sample showed much lower concentrations of HCCP (< 100 ppm). There were also some cases (Runs 1 and 3) in which the

2-hr samples were borderline in that they did show 99.99%, but the corresponding 6-hr sample results permitted calculation of the DRE to three decimal places (e.g., 99.997%). Calculation of the DRE is partly a function of exactly how much gas is sampled over the time period, but from these results it certainly cannot be said that 2 hr of sampling by MM5 is insufficient. On the other hand, 6 hr of sampling provides more assurance that the DRE can be computed to three decimal places. If a trial burn could consist of only one test, there would be little cost difference for a 2-hr versus a 6-hr test. However, if three replications are necessary, there would be some cost difference. Also, it must be realized that in analysis of samples of this type, there is always the possibility that unforeseen interferences will complicate the analysis and not allow detection limits to be as low as they might otherwise have been. In such cases, even 12 hr of sampling by MM5 might not be adequate. Unfortunately, such occurrences are almost impossible to predict beforehand.

Another method of sampling that can be used to increase the quantity of gas sampled is the Source Assessments Sampling System (SASS) train. Although much higher sampling rates are possible with a SASS train, as discussed in the Guidance Manual, the train is expensive, cumbersome to use, and subject to Cl^- corrosion. Most importantly, the SASS train was originally intended as a single point sampler, but would have to be used in these tests to traverse the stack as in Method 5. It is possible to use the SASS train, but, in our opinion, it is not nearly so practical as the MM5 train.

Although the MM5 train was used in this project, several problems were encountered in the first series of tests. Slight modifications eliminated most of these problems. The first problem was that a 6-hr sampling time, and even 2-hr, can lead to collection of large amounts of condensate in the impingers, with excessive carryover or frequent interruptions to empty the impingers, when sampling a high moisture gas stream from a wet scrubber. For this reason, the train used in the second set of testing incorporated a large condensate collection bottle, and larger impingers have been purchased for future work.

Another problem was the XAD-2 resin cartridges. The resin itself was not a problem, but the frit at the bottom tended to plug up, requiring changing the cartridge. Based on recommendations by others, who have had similar problems, a small 3.175-mm (1/8-in.) hole was drilled in frits and covered with glass wool, and the cartridge was repacked with the resin. This alleviated the problem. Others doing this type of testing should be prepared to take similar action, or do so before it becomes necessary in the field.

The frit that backs up the filter in the MM5 train was also a problem since several of them broke during sampling. Possible causes have been investigated with little success. The problem had not previously occurred in numerous tests at other sites. No clear reason for this problem could be identified. It may have been unique to this test site, but, if not, it would be a major problem when a single train is being used to determine both particulate and POHC emissions. Breakage of the frit (and filter) does not necessarily impact on determination of POHCs, but would make it impossible to determine particulate concentration.

The protocol is not specific about the arrangement and contents of each individual impinger. Therefore, a diagram of the train used in Runs 7 through 9 is presented in Figure 6, and is in accordance with the A. D. Little manual. It should be noted that the first impinger was in a reversed position in order to prevent any runback of condensate into the filter holder. Also, the inlet to the large condensate collection bottle does not extend down into the bottle, so that any possibility of carryover is minimized. If the A. D. Little manual had been available at the time the tests were conducted, the HCl emissions would have been sampled by placing another impinger containing caustic solution, in the train just ahead of the H_2O_2 impinger. Of course, both the condensate and caustic would have had to be analyzed for Cl^- content. In this way, a much better measure of the HCl emissions would be obtained.

Measurements of HCl in the first series of tests were made using the 1977 method given in the Guidance Manual. Briefly, this method is similar to EPA Method 6 (SO_2)[6] wherein a heated probe with a glass wool plug (for particulate removal) is connected to a series of midget impingers containing caustic solution. After sampling, the contents of the impingers are analyzed for Cl^-, and so also is the plug and probe rinse. This technique might be suited for the determination of the HCl content of hot gas streams (e.g., municipal incinerator), but is not suited for sampling high moisture gas streams from wet scrubbers, if the purpose is to determine HCl emissions. The reason for this is that often the use of a wet scrubber will result in the carryover of some liquid or solid particles that contain chloride salts such as NaCl. These chloride salts will affect the HCl analysis, being counted as HCl, especially from the plug and probe rinse. The advantage of using the MM5 train, as recommended by A. D. Little, is that any chloride-containing particulate will be collected on the filter and, therefore, not affect Cl^- analysis of the condensate and caustic impinger. Likewise, any droplets that enter the MM5 probe will most likely be evaporated, releasing any dissolved HCl and forming particulate from any chloride salts.

Finally, it is recommended that the protocol needs to address integrated gas sampling further. This sampling technique is just as important as the MM5 train because analysis of integrated gas samples is the basis for calculating DRE for any volatile POHCs.

The Guidance Manual contains no information on the protocol for integrated gas sampling, but the A. D. Little manual discusses two options for such sampling. The first option involves taking integrated gas samples in 10- to 30-liter bags. However, the A. D. Little manual does not mention that such bag samples should be analyzed within a period of days, since certain constituents in the sample are capable of permeating through the bags. The gas sampling bags are also cumbersome to use in the field, require careful handling, and tend to leak.

The second option for gas sampling presented in the A. D. Little manual involves sampling with 2-liter gas bulbs. However, these are only grab samples, making reliance on them questionable for evaluating DRE.

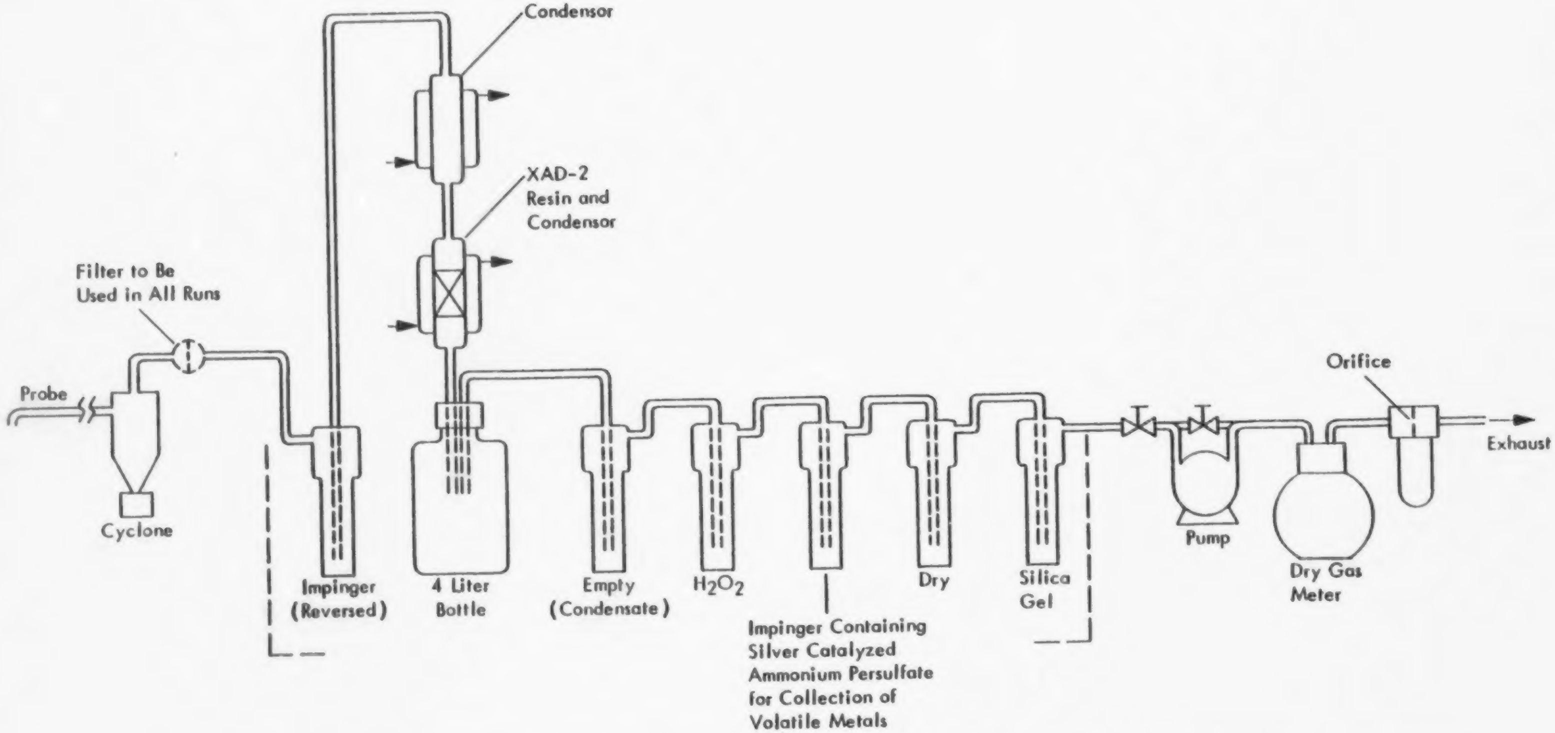

Figure 6. Schematic illustration of sampling train used at Cincinnati MSD incinerator tests.

For the above reasons, it is concluded that different procedures should be investigated for integrated gas sampling. One option is EPA Method 25[4] which was used during the second series of tests at Cincinnati. Another option is presented for consideration in Appendix K. Also, as mentioned earlier, work is in progress for EPA on a special volatile organic sampling train.

The preceding discussion covers most of the more important aspects of sampling protocol included as part of this project. Some additional important points about sampling need to be brought out relative to the manual prepared by A. D. Little, and the Guidance Manual.

A. D. Little Manual--

It is quite important to anyone considering a trial burn that the A. D. Little manual clearly allows one single MM5 train to be used for:

- POHC's (semivolatile)
- Particulate
- HCl
- Vaporous metals

However, the manual indicates (page 15) that the trial burn will consist of three separate tests under each set of operation conditions, presumably for each waste. This, of course, increases the length of any test period and, as mentioned earlier, would require a rather large quantity of waste.

On page 15 of the A. D. Little manual, it is recommended that the permit writer select at least one POHC from the 20 most abundant organic components and that other POHCs selected be present in the waste at 1,000 ppm or higher. MRI does not disagree with this recommendation; however, it is not consistent with the ranking and selection methodology in the Guidance Manual and it would mean that any other compounds that are difficult to incinerate would not be selected as POHCs, if present at less than 1,000 ppm.

Emission of vaporous metals is discussed in the A. D. Little manual and is based on analysis of a special impinger used in the MM5 train. However, it would seem logical to expect that some of these vaporous metals might be captured in the condensate preceding the special impinger. An analysis of the condensate for these metals should be included according to later discussions with EPA.

Guidance Manual--

A number of important points need to be emphasized about the protocol in the Guidance Manual, even though most of them have been discussed in other sections of this report.

The Guidance Manual states (page 54) that if the most difficult to incinerate POHCs are destroyed (> 99.99% DRE), then it can be assumed that others less difficult to incinerate will also be destroyed. But on another page (page 56), the manual says that the waste cannot contain any POHCs other than those in the permit. This is consistent with the regulation, but, as pointed out earlier, could certainly increase the number of trial burns required. If the first statement is acceptable, why is the second statement so restrictive?

Another portion (page 74) of the Guidance Manual addresses similarity of wastes and presents several criteria for assessing similarity. These may all be reasonable criteria but it is not likely, in many cases, that an operator would be able to have or obtain such data in any reasonable period of time on each waste received. Thus, again the operator (and EPA) is forced to assume that all wastes received meet those criteria, unless it is known otherwise.

A few other important points about the protocol in the Guidance Manual are:

- The manual seems to be saying (page 57) that one test at any given set of conditions is acceptable, and this conflicts with the three tests indicated in the A. D. Little manual.
- There is little reason to monitor air flow rate (pages 63 and 112) and many plants are not equipped to do so. Continuous O_2 monitoring would be much more useful.
- The Guidance Manual allows determination of HCl removal efficiency based on input of organically bound Cl in the waste (page 88). There is a potential problem here in nomenclature, if the waste contains significant amounts of inorganic chlorides (especially watery wastes), as discussed previously in this chapter.

A conclusion from the above discussion is that the Guidance Manual now needs to be revised in order that it be consistent with the A. D. Little manual, or it should specifically refer the reader to the latter manual.

Analysis

Evaluations of the analysis protocol were carried out for all of the testing done on this project but with much emphasis on the most complex area, the analysis of POHCs. Methods used for the POHC analysis (and metals) and recommended changes in the protocol are presented in detail in Appendix K. Therefore, this section will discuss only the major deviations in protocol for POHCs and metals analysis, after a few important points are brought out about evaluation of other analysis protocols.

One of the problems found with the analysis specified in the Guidance Manual and the A. D. Little manual (page 86) is determination of moisture in liquid wastes high in organics content. For such wastes, moisture should be determined by some other method (e.g., Karl Fischer titration) because the methods specified in the protocol are not applicable.

A second problem relates to Cl^- analysis for determining HCl emissions. The MM5 sampling procedure recommended in the A. D. Little manual should eliminate this problem.

Only minor problems occurred in any of the other analysis protocols with the exception of metals and POHCs as mentioned earlier. But analysis of samples for major constituents (non-POHCs) was very difficult, primarily because high molecular weight compounds may not be chromatographable (e.g., paint sludge polymers). Somewhat related to this, the A. D. Little manual does recommend a "survey analysis" of waste feed samples (page 90) to identify major types of organic compounds. Those analyses consist of TCO, Grav, infrared, probe MS procedures, and GC/MS. Only the latter two of these actually identify specific compounds (and both were tried without total success in attempting to identify the major organic components of the complex waste feed samples obtained in this project). Therefore, it is our opinion that the survey analysis will be of limited usefulness and that it would be more worthwhile to carry out only the "directed analysis" to semiquantitatively determine all compounds present in the sample that are listed POHCs.

Metals analysis of the waste feed samples presented another difficult problem, as mentioned earlier, since the semisolid phase present in the samples could not be effectively digested by the specified techniques. The EPA presently is investigating and developing better digestion methods for such cases.

The A. D. Little manual (page 16) shows that particulate from the MM5 train is to be extracted and analyzed for both metals and POHCs. However, the manual does not indicate how it is to be extracted for the metals analysis.

Analysis of POHCs in all of the different types of samples was the most complex part of this project, and concentrated on POHCs in the waste feed samples, gas bags, and MM5 train samples. These are discussed in more detail in Appendix K, but some of the major difficulties and changes necessary in the protocol are summarized below.

In analyzing for volatile POHCs in the waste feed samples, the polyethylene glycol method was used, because the samples would not disperse in water. The PEG method is mentioned as an option in the A. D. Little manual, but details are not provided and should be included.

Integrated Gas Sample Analysis--

Integrated gas samples taken in the first series of tests were analyzed by passing the gas sample through a Tenax trap and then heat-desorbing the trap onto the GC column, after which it was analyzed as specified by the procedures in the A. D. Little manual (Method A101). But, in the second series of tests, the Tenax trap was heat-desorbed onto a capillary column, because it gave better sensitivity and better resolution. Neither of these techniques is adequately described in the manual. Also, as mentioned earlier, a better integrated gas sampling technique is needed or, alternatively, the development of the volatile organic sampling train (VOST).

Analysis of MM5 Train Samples--

One of the MM5 train samples is the probe rinse, which consisted of a combined sample from rinsing of the probe with water, acetone, and cyclohexane. The resulting biphasic mixture was shaken, after which the cyclohexane phase (with some acetone) was separated and analyzed. The problem is that it is not known if this is a good technique for recovering POHCs, so such techniques need to be developed and specified in the protocol.

An important revision that could be suggested in the MM5 train is to rearrange it so that condensate is collected before the gases pass through the resin. This would help minimize the problem of wet resin, but the main reason for the suggested change is that the POHC absorption efficiency of the resin might be impaired due to the large amount of water. Further, any POHCs escaping collection in the resin may not remain in the condensate, because they might be purged out by the high gas flow in the condensate collection impingers. In order to investigate this, MRI plans to carryout further test work with XAD resin traps located both before and after condensate collection. Discussions with EPA indicate that the XAD resin trap located before condensate collection should be retained.

Another question about the MM5 train is that it was arranged so that all condensate flowed through the XAD-2 resin, which necessitated a deviation from the analysis specified in the A. D. Little manual (P024B). That is, the resulting resin was very wet, and the water must be at least partially removed prior to extraction. For this test program, a benzene-methanol mixture was chosen to prerinse the resin and remove water. The resin was then extracted with the same mixture per the method. The prerinse and extract were combined, after which the benzene portion was separated, concentrated, and analyzed.

Subsequent to this effort, an EPA authority on sampling and analysis (Larry Johnson) indicated that methylene chloride should have been used as the extracting solvent. Since all analyses were already completed and there were no samples left, an experiment was conducted to determine the difference in the recoveries of the two extraction procedures (i.e., benzene-methanol mixture and methylene chloride). Experimental results indicated that methylene chloride yielded better recoveries for most of the selected POHCs. This aspect is discussed in more detail in Appendix K.

Scrubber Effluent and Bottom Ash Analysis--

The only problem noted in regard to these two water samples was that if they are to be analyzed for volatile POHCs, a sample collection technique needs to be specified that overcomes the fact that in taking hot liquid samples it is impossible to avoid "head space" in the sample container, due to contraction of the liquid. In fact, if the hot sample is taken without any head space, a vacuum develops in the container during cooling, with probable loss of volatiles.

ECONOMIC ASPECTS OF TRIAL BURNS

One of the objectives of this program was to assess the economic impacts of a trial burn on the incinerator operator in terms of cost of conducting the trial burn including, associated costs such as increased fuel or power usage. Since the EPA Guidance Manual on trial burns does not specify the number of runs, or the duration of each run, or the number of POHCs to be selected and also because of other unresolved issues on sampling analysis procedures, as discussed through the report, there is a need to first define a "trial burn."

The approach taken involves defining or scoping the trial burn at three levels starting with a simple sampling and analysis program with a minimum number of tests and minimum analyses and proceeding to two more complex levels of testing. Tables 21, 22, and 23 attempt to characterize these three levels of testing for the trial burn options.

In addition to the obvious differences between Tables 21, 22, and 23 with respect to the number of runs, duration of each run, type of analysis, etc., a trial burn can also be complicated by the type of waste burned and the configuration of the incineration facility. For example, a homogeneous waste makes analysis simpler than a multiphasic waste. Also, the type of POHC selected and its concentration in the waste can dictate the level of complexity in the analysis effort which could have direct impact on cost. Similarly, the configuration of the facility determines the ease of setting up sampling points and conducting the sampling activity. Therefore, this discussion on economic impact is intended more to demonstrate the possible variation in the cost of conducting a "trial burn" rather than to come up with definitive figures.

Based on the experience gained from this project and other sampling and analysis activities, the Level 1 Scale of trial burn shown in Table 21 is estimated to require in the range of 900 to 1,200 person-hours to conduct the sampling and analysis, data interpretation, and report preparation. This estimate does not include travel related costs and site preparation costs such as scaffolding, truck rentals, etc. Although GC/MS user charge is not included in this estimate, other costs of analysis of samples such as sample preparation, extraction, etc., are included. On the same basis, the Level 2 option could require in the range of 1,200 to 1,500 person-hours, not including other direct costs indicated above (i.e., travel, site preparation, and user charge associated with GC/MS time). For Level 3, the cost would depend upon the number of operating conditions and the extent of fugitive emissions sampling that is planned; this latter aspect, of course, would be highly specific to each site.

Another aspect which could impact on costs is "fuel usage." During the time of the Cincinnati MSD tests, fuel oil was burned at night and during times when sampling was not being done, instead of burning the waste itself as per normal practice. This was required in order to conserve waste, because there was not enough waste of the same type to cover the 6- and 3-day test periods. Therefore, it is imperative that the test sites have adequate amounts of waste for the trial burn.

Power usage was also monitored during the tests at Cincinnati to determine the incremental impact of usage during the trial burn. Since the only additional power usage sources were the trailer and the small pumps on the sampling train, no change in the usage rates was seen. Therefore, it is not believed that a trial burn would impose additional power costs other than those encountered during normal operation of the incineration facilitiy.

In summary, this section provides a framework from which to assess costs and to bring out those aspects of a trial burn that could impact on the cost of conducting a trial burn.

TABLE 21. TRIAL BURN OPTION - LEVEL 1

Number of Runs: 2
Duration of Each Run: 2-1/2 hr
Sample Streams for Analysis: waste, fuel oil, quench water, stack gas

	Type of sampling	Type of analysis
Waste	Sample every half-hour and integrate over 2 hr period	2 POHCs, chloride, HHV, moisture content
Fuel oil, quench water	1 grab sample of each at any point in 2 hr period	2 POHCs
Stack gas	EPA Modified Method 5 run	2 POHCs; particulate conc., chloride removal efficiency, As, Se, Hg conc.
	Orsat for O_2, CO_2	O_2, CO_2
	Integrated gas sample (EPA Method 25)	Analyze for volatile POHCs if either of the two selected POHCs are volatile

Note: It is estimated that the above option would require 900-1,200 person-hours not including other direct costs such as travel, site preparation, etc.

TABLE 22. TRIAL BURN OPTION - LEVEL 2

Number of Runs: 3
Duration of Each Run: 2-1/2 hr
Sample Streams for Analysis: waste, fuel oil, quench water, scrubber effluent, bottom ash, stack gas

	Type of sampling	Type of analysis
Waste	Sample every 15 min and integrate over 2-1/2 hr period	3 POHCs, chloride, HHV, moisture content, ultimate/proximate analysis
Fuel oil and quench water	1 grab sample of each at any point in 2-1/2 hr period	3 POHCs
Scrubber effluent	Composite 3 grab samples	EP toxicity
Bottom ash	1 sample during sluicing preferably at the time of stack sampling	EP toxicity
Stack gas	EPA Modified Method 5 run	3 POHCs; particulate conc., chloride removal efficiency, As, Se, Hg conc.
	Orsat for O_2, CO_2	O_2, CO_2
	Integrated gas sample (EPA Method 25)	Analyze for volatile POHCs if any of 3 POHCs selected are volatile

Note: It is estimated that the above option would require 1,200-1,500 person-hours not including other direct costs such as travel, site preparation, etc.

TABLE 23. TRIAL BURN OPTION - LEVEL 3

Number of Runs: 3 runs at each of several operating conditions (i.e., different operating temperature or residence times)
Duration of Each Run: 2-1/2 hr
Sample Streams for Analysis: waste, fuel oil, quench water, bottom ash, scrubber effluent, stack gas, fugitive emissions at appropriate locations in plant

	Type of sampling	Type of analysis
Waste	Sample every 15 min and integrate over 2-1/2 hr period	5 POHCs, chloride, HHV, moisture content, trace metals, ultimate/proximate analysis
Fuel oil and quench water	1 grab sample of each at any point in 2-1/2 hr period	5 POHCs
Bottom ash	1 sample during sluicing preferably at the time of stack sampling	EP toxicity, 5 POHCs, chloride
Scrubber effluent	Sample every 15 min and integrate over 2-1/2 hr period	EP toxicity, 5 POHCs, chloride
Stack gas	EPA Modified Method 5 run	5 POHCs; particulate conc., chloride removal efficiency, As, Se, Hg conc., and trace metals in particulate
	Orsat for O_2, CO_2	O_2, CO_2
	Integrated gas sample (EPA Method 25)	Analyze for volatile POHCs if any of 5 POHCs selected are volatile
	Continuous monitoring for CO, NO_x, total HC	CO, NO_x, total HC conc.

Note: It is estimated that the above option for 3 runs at one operating condition would require 2,000-2,300 person-hours not including fugitive emissions, and other direct costs such as travel, site preparation, etc.

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APPENDIX A

GENERAL ANALYSIS RESULTS FOR WASTE FEED ANALYSIS

Results of waste feed analysis are presented in Tables A-1 to A-6 of this appendix.

TABLE A-1. GENERAL ANALYSIS RESULTS FOR 6-HR WASTE FEED SAMPLES - RUNS 1-6

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Viscosity (SUS at 100°F)	40	70	40	40	39	39
Flash point (°C)	31.1	31.7	18.3	40	28.9	12.2
Htg. value (Kcal/Kg)	2,750	3,355	5,472	3,316	5,527	5,480
(Btu/lb)	(4,949)	(6,039)	(9,848)	(5,968)	(9,948)	(9,864)
Water content (wt. %)[a]	65.30	57.20	33.54	57.47	31.66	28.61
Proximate analysis as received (wt. %)						
Wt. loss at 105°C[b]	NA	NA	NA	NA	NA	NA
Wt. loss at 750°C[c]	98.92	98.38	98.48	98.90	98.69	97.60
Ash	0.93	0.22	1.29	0.47	0.25	0.47
Fixed carbon[d]	0.15	1.40	0.23	0.63	1.06	1.93
Ultimate analysis as received (wt %)						
Carbon	25.81	35.66	48.13	29.26	53.18	45.13
Hydrogen	10.32	9.21	9.59	9.85	10.38	10.03
Nitrogen	0.66	0.77	0.50	0.75	0.65	0.56
Chlorine	2.91	3.13	7.08	3.46	5.88	6.97
Sulfur	0.29	0.39	0.10	0.43	0.38	0.35
Oxygen[d]	60.01	50.84	34.60	56.25	29.53	36.96

[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

NA - Not analyzed.

TABLE A-2. GENERAL ANALYSIS RESULTS FOR 6-HR WASTE FEED SAMPLES - RUNS 7-9

	Run 7	Run 8	Run 9
Viscosity (SUS at 100°F)	54	44	39
Flash point (°C)	4.4	4.4	1.7
Htg. value (Kcal/Kg)	6,261	6,011	7,090
(Btu/lb)	(11,269)	(10,819)	(12,761)
Water content (wt. %)[a]	13.52	14.86	4.65
Proximate analysis as received (wt. %)			
Wt. loss at 105°C[b]	80.16	80.08	76.90
Wt. loss at 750°C[c]	17.11	16.35	21.25
Ash	1.56	1.37	0.21
Fixed carbon[d]	1.17	2.20	1.64
Ultimate analysis as received (wt %)			
Carbon	56.35	50.34	61.26
Hydrogen	8.82	8.60	8.58
Nitrogen	0.63	0.57	0.68
Chlorine	15.50	15.08	15.87
Sulfur	0.23	0.21	0.20
Oxygen[d]	18.47	25.20	13.41

[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

TABLE A-3. GENERAL ANALYSIS RESULTS FOR WASTE FEED SAMPLES - RUN 2

	Integrated samples			
	6-hr	2-hr-A	2-hr-B	Grab sample
Viscosity (SUS at 100°F)	70	38	38	38
Flash point (°C)	31.7	27.8	29.4	24.4
Htg. value (Kcal/Kg)	3,355	6,816	3,522	4,360
(Btu/lb)	(6,039)	(12,267)	(6,339)	(7,847)
Water content (wt. %)[a]	57.20	18.58	50.12	47.04
Proximate analysis as received (wt. %)				
Wt. loss at 105°C[b]	NA	NA	NA	NA
Wt. loss at 750°C[c]	98.38	98.17	98.63	97.49
Ash	0.22	0.21	0.23	0.39
Fixed carbon[d]	1.40	1.62	1.14	2.12
Ultimate analysis as received (wt %)				
Carbon	35.66	59.00	35.62	43.39
Hydrogen	9.21	10.16	9.03	8.53
Nitrogen	0.77	0.51	0.76	0.75
Chlorine	3.13	8.22	3.17	3.99
Sulfur	0.39	0.38	0.41	0.01
Oxygen[d]	50.84	21.73	51.01	43.33

[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

NA - Not analyzed.

TABLE A-4. GENERAL ANALYSIS RESULTS FOR WASTE FEED SAMPLES - RUN 4

	Integrated samples			
	6-hr	2-hr-A	2-hr-B	Grab sample
Viscosity (SUS at 100°F)	40	40	35	38
Flash point (°C)	40	27.2	61.7	26.7
Htg. value (Kcal/Kg)	3,316	3,773	4,454	5,139
(Btu/lb)	(5,968)	(6,790)	(8,017)	(9,249)
Water content (wt. %)[a]	57.47	50.19	48.90	35.10
Proximate analysis as received (wt. %)				
Wt. loss at 105°C[b]	NA	NA	NA	NA
Wt. loss at 750°C[c]	98.90	98.60	97.84	98.95
Ash	0.47	0.43	2.16	0.16
Fixed carbon[d]	0.63	0.97	0.00	0.89
Ultimate analysis as received (wt %)				
Carbon	29.26	29.51	40.71	53.57
Hydrogen	9.85	9.87	8.81	9.55
Nitrogen	0.75	0.79	0.76	0.66
Chlorine	3.46	4.05	4.74	5.17
Sulfur	0.43	0.29	0.08	0.40
Oxygen[d]	56.25	55.49	44.90	30.65

[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

NA - Not analyzed.

TABLE A-5. GENERAL ANALYSIS RESULTS FOR WASTE FEED SAMPLES - RUN 7

	Integrated samples			
	6-hr	2-hr-A	2-hr-B	Grab sample
Viscosity (SUS at 100°F)	54	58	55	48
Flash point (°C)	4.4	1.7	1.7	1.7
Htg. value (Kcal/Kg)	6,261	5,370	5,539	5,377
(Btu/lb)	(11,269)	(9,665)	(9,969)	(9,677)
Water content (wt. %)[a]	13.52	22.34	22.54	22.44
Proximate analysis as received (wt. %)				
Wt. loss at 105°C[b]	80.16	80.49	80.31	79.89
Wt. loss at 750°C[c]	17.11	16.00	16.78	16.16
Ash	1.56	3.11	2.81	2.99
Fixed carbon[d]	1.17	0.40	0.10	0.96
Ultimate analysis as received (wt %)				
Carbon	56.35	46.72	44.55	43.05
Hydrogen	8.82	8.63	9.00	8.84
Nitrogen	0.63	0.60	0.65	0.63
Chlorine	15.50	13.03	13.45	13.61
Sulfur	0.23	0.22	0.23	0.22
Oxygen[d]	18.47	30.80	32.12	33.65

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[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

TABLE A-6. GENERAL ANALYSIS RESULTS FOR WASTE FEED SAMPLES - RUN 8

	Integrated samples			
	6-hr	2-hr-A	2-hr-B	Grab sample
Viscosity (SUS at 100°F)	44	41	36	36
Flash point (°C)	4.4	1.7	-1.1	1.7
Htg. value (Kcal/Kg)	6,011	5,749	5,983	5,997
(Btu/lb)	(10,819)	(10,348)	(10,769)	(10,794)
Water content (wt. %)[a]	14.86	17.42	12.57	12.12
Proximate analysis as received (wt. %)				
Wt. loss at 105°C[b]	80.08	79.07	80.47	80.94
Wt. loss at 750°C[c]	16.35	16.79	16.00	15.57
Ash	1.37	1.69	1.10	1.05
Fixed carbon[d]	2.20	2.45	2.43	2.44
Ultimate analysis as received (wt %)				
Carbon	50.34	48.57	50.93	50.31
Hydrogen	8.60	8.63	8.73	8.50
Nitrogen	0.57	0.57	0.55	0.66
Chlorine	15.08	14.80	16.23	13.54
Sulfur	0.21	0.24	0.20	0.22
Oxygen[d]	25.20	27.19	23.36	26.77

[a] Water content determined by Karl Fischer titration.

[b] Weight loss at 105°C is referred to as "moisture" in analysis of solid fuels.

[c] Weight loss at 750°C is referred to as "volatile matter" in analysis of solid fuels.

[d] Calculated by difference.

APPENDIX B

DESCRIPTION OF ANALYSIS FOR MAJOR CONSTITUENTS

Several analytical techniques have been applied in an attempt to characterize the major organic components in Waste Feed Samples 1-6, and, in particular, Sample WF(6)-2. The techniques that were used included the following:

- Purge-trap-desorb GC/MS analysis of a polyethylene glycol (PEG) extract of the waste for volatiles.
- Fractional distillation followed by infrared spectroscopic analysis of the collected fractions (GC/MS analysis of two fractions for volatiles.)
- Direct GC/MS on-column injection to analyze for volatiles.
- Solvent dissolution followed by glass capillary GC/MS analysis for semivolatiles.
- Thin-layer chromatographic analysis of the waste.
- Direct insertion probe mass spectrometric analysis of the waste residue. (i.e., residue remaining after evaporation of volatiles with N_2).
- Liquid chromatographic separation of the waste (refractive index detector) followed by direct insertion probe mass spectrometric analysis of two collected fractions.
- Proximate analyses (elemental composition, heating value, and water by Karl Fischer titration).

A brief description of each of the techniques used to characterize the samples and a summary of the results are presented below.

TECHNIQUES TO CHARACTERIZE THE MAJOR COMPONENTS IN THE WASTE FEED SAMPLES

Purge-Trap-Desorb GC/MS Analysis

A portion of the waste was dissolved in polyethylene glycol and an aliquot spiked into reagent water along with the internal standards. The sample was analyzed by the purge-trap-desorb technique according to EPA Method 624 (Method A101--ADL report).

On-Column GC/MS Analysis

The purpose of the on-column injection GC/MS analysis of the sample was to search for the presence of volatile compounds in the waste feed sample which may not have purged well and were not detected using the purge-trap-desorb technique. The on-column injection technique gives a true indication of the relative amounts of volatile organic components of the sample.

The samples were analyzed by injecting approximately 0.1 µl into the injection port of the GC. Larger amounts would overload the column and mass spectrometer. Although an internal standard could not be added to the sample using this technique, the compounds observed could be approximately quantified by comparing the peak areas to the areas of compounds which do purge completely and which were accurately quantified during the purge-trap-desorb analysis of the sample.

The total ion chromatograms from analysis of the sample by the purge-trap-desorb technique and the direct injection technique are compared in Figures B-1 and B-2, respectively. The appearance of the two chromatograms is significantly different. Several of the early-eluting peaks are higher relative to toluene, the highest peak in both samples, when the sample was injected directly on-column. These are polar compounds which do not purge well from water. Such compounds can be accurately quantified when calibration standards containing these compounds are analyzed because the mass spectrometric response factors used to quantify the compounds take the purging efficiences into account. However, many of the compounds were not analyzed in calibration standards because they are not POHCS. Therefore, their concentrations were estimated from comparison to peak heights of compounds such as toluene, which do purge completely.

Some of the compounds that were detected using on-column injection that were not prominent during the purge-trap-desorb analysis include methanol, diethyl ether, acetone, ethyl acetate, acetic acid, some esters and a few additional compounds. Toluene gave nearly the largest peak using both techniques although methanol may be the major compound from the results of the direct injection analysis of the sample. However, no predominant amounts of any other compounds were detected using this technique compared to purge-trap-desorb. A few nonpolar compounds appeared in the purge-trap-desorb analysis which were masked in the direct injection analysis including 1,2-dichloroethane, dimethyl disulfide, benzene, and cyclohexane. The total estimated amounts of all the volatile compounds in Sample WF(6)-2 are provided in Table B-1. As can be seen, the chromatographable volatile organic compounds account for about 11% of the total sample composition and suggests that most of the sample still needs to be accounted for.

Fractional Distillation/Infrared Analysis

The purpose of the fractional distillation/infrared spectroscopy analysis was to search for significant quantities of material, for example water, which is not chromatographable, not organic, or not readily detectable using GC/MS techniques.

For this experiment, a 15.7 g homogenized aliquot of Sample WF(6)-2 was added to a 25 ml round bottom flask. To the flask was inserted a Vigreaux column fitted with a thermometer. A condenser was attached to the side arm of the Vigreaux column for condensation of the distilled vapors. The condensed fractions were collected in vials as they dripped from the condenser tube.

Nine different fractions were collected during the distillation. The fractions ranged in weight from 0.56 to 2.1 g. Many of the fractions contained two layers suggesting collection of an aqueous phase and an organic phase. Most of the biphasic samples consisted of a clear layer on the bottom and a layer on top which changed from a light to dark brown color as the distillation progressed. The bottom layer also displayed a yellowish hue near the end of the distillation.

The first fraction was collected at a temperature of about 70°C. The temperature then increased to a maximum of about 110°C when the entire sample had distilled except for 0.33 g of residue.

Each of the collected fractions, including each phase of the biphasic samples was analyzed on a Perkin Elmer Model 283 infrared spectrophotometer. Each sample was analyzed by inserting a few microliters of sample between a sodium chloride salt plate. Examination of the resulting IR spectra suggested that the fractional distillation yielded some, but not significant, fractionation of the sample. The bottom layers, which ranged from 50 to 95% of the sample volume in the collected fractions, contained significant amounts of water as indicated from O-H stretch in the IR spectra. The IR spectra of the top layers were not particularly informative. The IR spectra were quite complex, but did reveal C-Cl bonds in the early top layer fractions and aromatic hydrocarbons (toluene) in the later top layer fractions. The residue, which was also analyzed, was complex but suggested higher MW alcohols as the principal constituent.

Two of the fractions collected from the fractional distillation, the first fraction (single phase), and the top phase of the fifth fraction were analyzed by on-column injection GC/MS. The total ion chromatogram of the first fraction, as shown in Figure B-3, appears very similar to the total ion chromatogram obtained from injection of the whole sample (Figure B-2) except that this sample was significantly enriched in benzene (Scan 275). This result suggests that fractional distillation is only marginally effective in separating such a complex mixture. The GC/MS analysis of the top layer of fraction five showed that this sample was enriched in the higher molecular weight components as shown in Figure B-4. The relative sparseness of peaks in the early portion of the chromatogram revealed the presence of ethanol, methyl ethyl ketone, and 1,4-dioxane, which were not apparent in the other samples.

In summary, the fractional distillation and infrared analysis of the resulting fractions suggested the presence of substantial quantities of water in the waste feed samples which coincide with the Karl Fischer titration data.

Semivolatile GC/MS Analysis

Analysis of the samples for semivolatile organic compounds was performed by dispersing a 5 g portion of the homogenized sample in hexane, further diluting 100 µl of this solution to 1.0 ml and spiking the 1.0 ml aliquot with 20 µg of D_{10}-anthracene internal standard (4,000 µg/g relative to the original sample). An aliquot of the resulting solution was analyzed on a capillary GC/MS system equipped with a split/splitless injector operated in the splitless mode. The total ion chromatogram of the sample in shown in Figure B-5. The chromatogram is quite complex at the beginning where most of the major compounds eluted. The sample is also characterized by very few late-eluting compounds. The components of this sample were not completely characterized as in the volatile fraction. However, several of the compounds were identified and their concentrations estimated as shown in Table B-2.

Altogether, a total of 75 peak heights were measured and compared to the peak height of the D_{10}-anthracene internal standard. Assuming that the peak height response of a given compound was equal to that of the D_{10}-anthracene internal standard, the total amount of semivolatile organic compounds in the sample would be about 12%. However, most of the types of compounds in the sample (excluding alkanes) would be expected to have a peak height response factor of less than one, thus increasing the amount of material measured in the sample. Figure B-6 shows the GC/MS analysis of a calibration standard containing equal amounts of about 130 different compounds including the D_{10}-anthracene internal standard. Only two compounds have peak heights greater than the D_{10}-anthracene. If we assume an average relative peak height response factor of 0.5, which is quite reasonable from inspection of Figure B-6, then the total amount of chromatographable semivolatile organic material in the sample amounts to at least 25%.

Thin-Layer Chromatographic Analysis

Thin-layer chromatographic (TLC) analysis was performed on samples WF(G)-1 and WF(2)-3B; these samples would be expected to be very similar to WF(6)-2. One other waste feed, 603TT(0), was also analyzed by TLC, but it is unrelated to waste feeds 1 to 6. The TLC analyses of WF(G)-1 and WF(2)-3B were not particularly informative. However, most of the material did move off the origin of the silica TLC plate suggesting that most of the organic material in the sample is not of high molecular weight (e.g., molecular weight > 400) and, also, not of high polarity.

Waste sample 603TT(0), which was a component of waste feed samples 7 to 9 but not 1 to 6, behaved considerably differently than WF(G) and WF(2) during TLC analysis. Much of the material in this sample did remain at the origin. The sample possessed an odor similar to styrene suggesting that the material remaining at the origin could be styrene oligomers, i.e., polystyrene.

Direct Insertion Probe Mass Spectrometry

During direct insertion probe mass spectrometry, several micrograms of the sample is transferred to a glass capillary tube and inserted directly into the ion source of the mass spectrometer. Some fractionation of the sample components occurs due to differential volatility (probe distillation) as the sample is slowly heated under vacuum in the source of the mass spectrometer. Therefore, this technique is useful for analyzing high molecular weight organic compounds which may not elute from a GC column.

Direct insertion probe mass spectrometry was performed on the residues from Sample WF(6)-2 and Sample 603TT(0). The data from sample WF(6)-2 was not particularly informative, probably because not much of the material in the residue was volatilizable. A phthalate mass spectrum was observed, which was probably bis(2-ethylhexyl)phthalate, although it may have been from a higher molecular weight phthalate. The bis(2-ethylhexyl)phthalate was observed during GC/MS analysis at a level of about 5,000 µg/g. The only other material observed during the probe analysis gave an alkane/alkene type of distribution of peaks with masses at m/z 41, 43, 55, 57, 69, 71, 83, 85, 97, 99, etc. This material distilled from the probe sample after phthalate and, thus, was not gas chromatographable. The source of the material may be waste oil. Although it was not possible to quantify this material, it probably amounted to less than 1% of the sample.

The probe mass spectrometric analysis of Sample 603TT(0) indicated a much different composition for the residue for this waste. This sample gave an elution pattern dominated by peaks at m/z 45, 59, 73, 89, and 103. Peaks at higher masses were very small but were always separated by either 14 or 16 mass units. This distribution of peaks suggests that this compound is a polyglycol ether with a structure consisting of repeating units of $(-CH_2-CH_2-O-CH_2-CH_2)_n$. These types of compounds are common industrial chemicals and are widely used in paints, packaging materials, fabric softeners, shampoos, and cosmetics.

Another peak observed during the probe distillation mass spectral analysis has not been identified. Although the compound must be of relatively high molecular weight because of its later elution during the probe mass spectral analysis, the only significant peaks were at m/z 30, 44, 58, 64, 72, and 73. The even masses suggest the compound contains an odd number of nitrogen atoms and may be a fatty amine of some type.

Liquid Chromatography/Direct Insertion Probe Mass Spectrometry

One other technique that was tested on waste feed WF(6)-2 was liquid chromatographic (LC) separation of the waste followed by manual collection of the LC eluent corresponding to observed peaks. To perform the separation, a sample of the waste was filtered through a 0.45 µm filter and mixed 1:1 with acetonitrile. The sample was injected onto a Waters Microbond C-18 column using 100% tetrahydrofuran (THF) as the mobile phase. The flow rate was 1.0 ml/min. The detector was a refractive index detector at an attenuation of x32.

Since the refractive index detector is quite insensitive, it was considered that any major peak which would appear would have to be a major constituent of the sample. The column eluent containing the peak would then be collected and analyzed by direct insertion probe mass spectrometry, possibly revealing the presence of a major non-volatile compound not observed during probe mass spectrometric analysis of the sample residue.

Only one major and one minor peak LC were observed following injection of the sample. Each of these peaks was collected, the solvent evaporated, and the residue analyzed by direct insertion probe mass spectrometry.

The mass spectrometric analysis of the LC fractions did not provide any additional information about the sample composition. The mass spectrometric analysis of the first peak gave characteristic ions of alkane/alkene and phthalates. Minor amounts of other compounds in these LC fractions gave ions at m/z 389, 403, 448 and 470 for one compound and m/z 133 and 385 for another compound. However, the compounds could not be identified. The second LC peak, which was much smaller than the first, gave only a phthalate mass spectrum. Apparently, the large LC peak corresponded to the elution of an unresolved envelope of peaks corresponded to a mixture of a large number of volatile and semi-volatile organic compounds.

Proximate Analysis

The proximate analyses, including elemental composition, heating value, and water content using a Karl Fischer titration were performed. Water was by far the major sample constituent and accounts for why the chromatographable organic compounds accounted for considerably less than half of the total composition of the sample.

Mass Balance Estimation

Based on the data discussed in the preceding sections, the following estimate of the mass balance of Sample WF(6)-2 can be made:

Constituent	Percent by Weight
Water	57
Volatile Organic Compounds	11
Semi-volatile Organic Compounds	25
Nonvolatile Organic Material	2 (estimate)
Total	95

The nonvolatile organic material is difficult to estimate because it may not even vaporize into the mass spectrometer during the probe analysis. The material may be inorganic and/or polymeric in nature, such as the residue that results from paint waste.

TABLE B-1. SUMMARY OF THE ESTIMATED AMOUNTS OF VOLATILE ORGANIC COMPOUNDS DETECTED IN SAMPLE WF(6)-2

Compound	Estimated amount (μg/g)
Methanol	10,000
Unknown	3,000
Methylene chloride	1,500
Acetone	4,000
Carbon disulfide	500
Dimethyl disulfide	500
Trichlorotrifluoromethane	200
Diethyl ether	8,000
Tetrahydrofuran	8,000
Chloroform	7,600
Dioxane	1,000
Butanal	3,000
Pentane	200
1,1,1-Trichloroethane	2,200
Carbon tetrachloride	2,200
Ethyl acetate	3,000
Methyl propanol	500
C_6 Alkene	800
Acetic acid	1,000
Butanol	4,000
C_6 Alkane	1,000
Trichloroethylene	500
Fatty acid ester	2,000
2-Ethoxyethanol	5,000
Benzene	3,000
Hexane	2,900
Propyl acetate	2,200
Methyl cyclohexane	1,000
Fatty acid ester	3,000
C_7 Alkane	300
Hexanone	2,000
Cyclohexanone	1,000
C_7 Alkane	1,500
C_7 Alkane	1,000
Tetrachloroethylene	1,800
Toluene	6,700
C_8 Cycloalkane	1,000
Chlorobenzene	3,000
Unknown	1,000
Cyclohexanemethanol	500
An ethoxy acetate ester	4,000
Xylene	3,000
C_7 Ketone	1,000
C_3 Alkylcyclohexane	1,200
Total	110,800
	= 11%

TABLE B-2. SUMMARY OF ESTIMATED AMOUNTS OF SELECTED SEMIVOLATILE ORGANIC COMPOUNDS DETECTED IN SAMPLE WF(6)-2

Compound	Estimated amount (μg/g)
Phenol	1,400
Dichlorobenzenes	1,200
Hexachloroethane	300
Isophorone	400
Dimethylphenol	150
Trichlorobenzenes	100
Naphthalene	700
Hexachlorobutadiene	200
Hexachlorocyclopentadiene	3,700
Hexachlorobenzene	200
Bis(2-ethylhexyl)phthlate	2,300
Dibutyl phthlate	200
Butyl benzyl phthalate	100
Chlorotoluene	1,700
Pentachlorbenzene	100
Aldrin	300
DDT	300
Isodrin	2,100
Unspecified alkanes	10,000
Alkyl cyclohexanes	3,000
Nonanol	3,000
Undecane	4,000
Alkyl benzenes	500
Phenoxy ethanol	1,000
Dodecanol	500
Octachlorocyclopentene	4,000
Adipates	1,000
	42,450
	= 4%

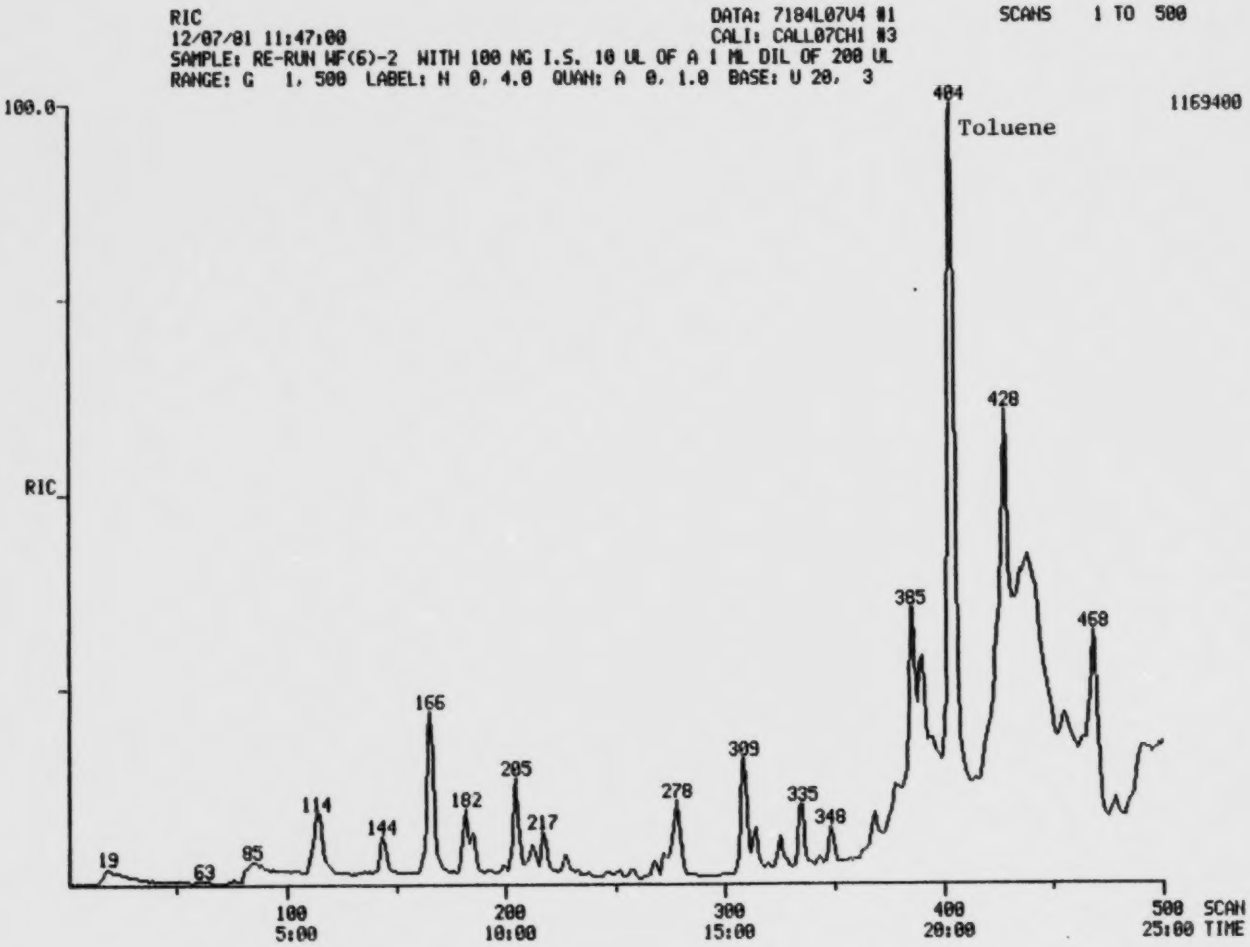

Figure B-1. Total ion chromatogram of purge-trap-desorb GC/MS analysis of homogenized sample WF(6)-2 for volatiles.

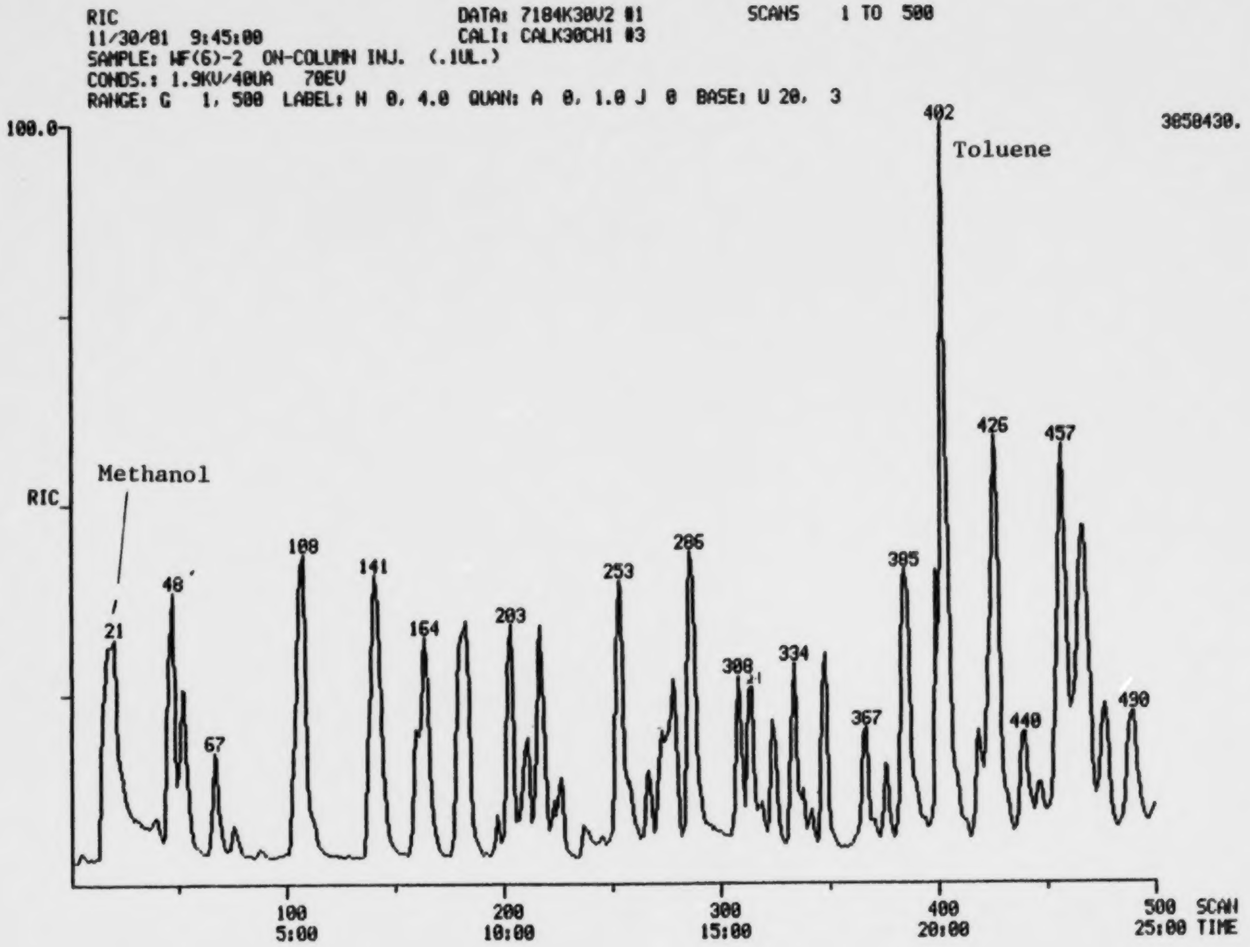

Figure B-2. Total ion chromatogram from on-column injection GC/MS analysis of homogenized sample WF(6)-2 for volatiles.

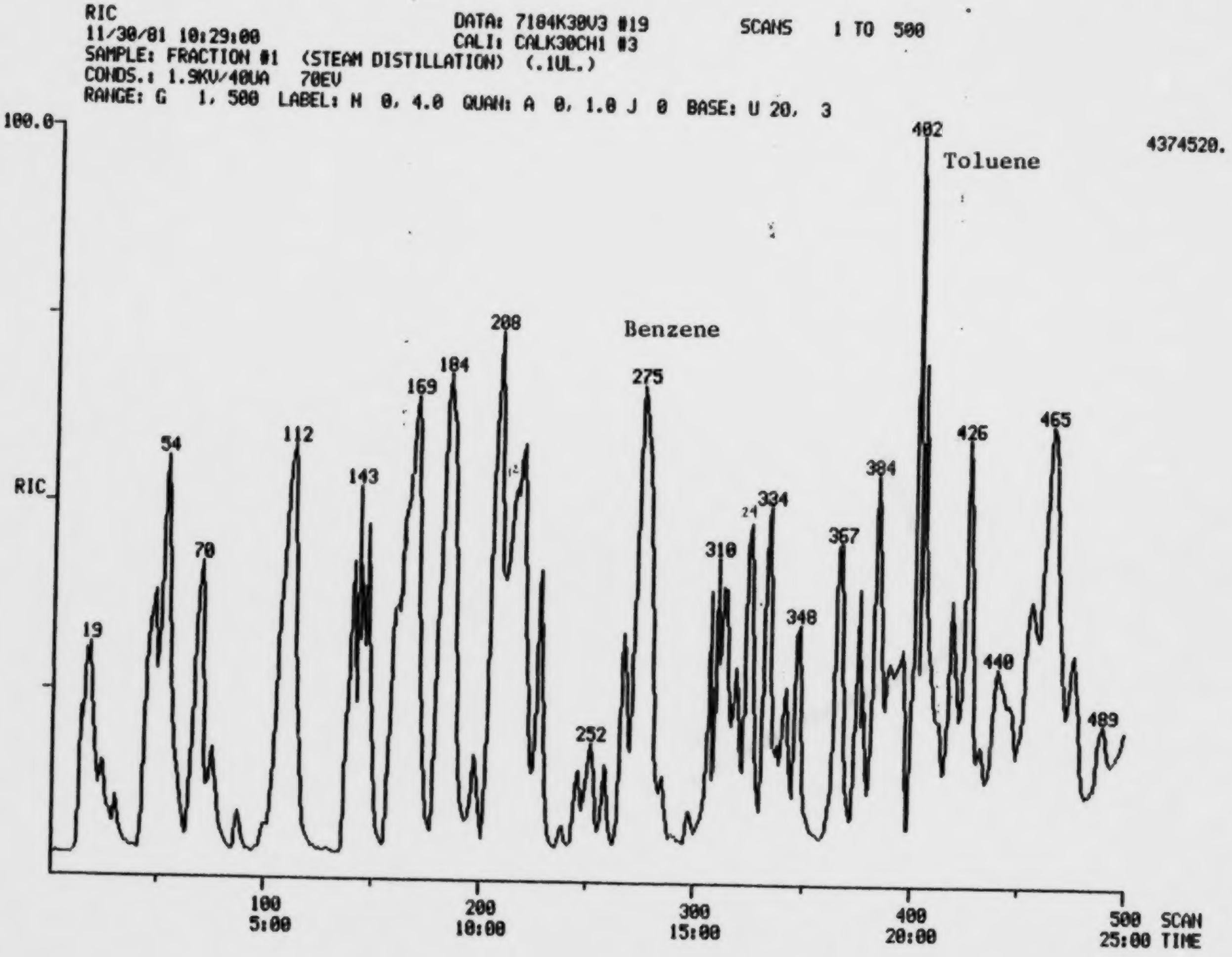

Figure B-3. Total ion chromatogram from on-column injection GC/MS analysis of fractional distillation of fraction No. 1 for volatiles.

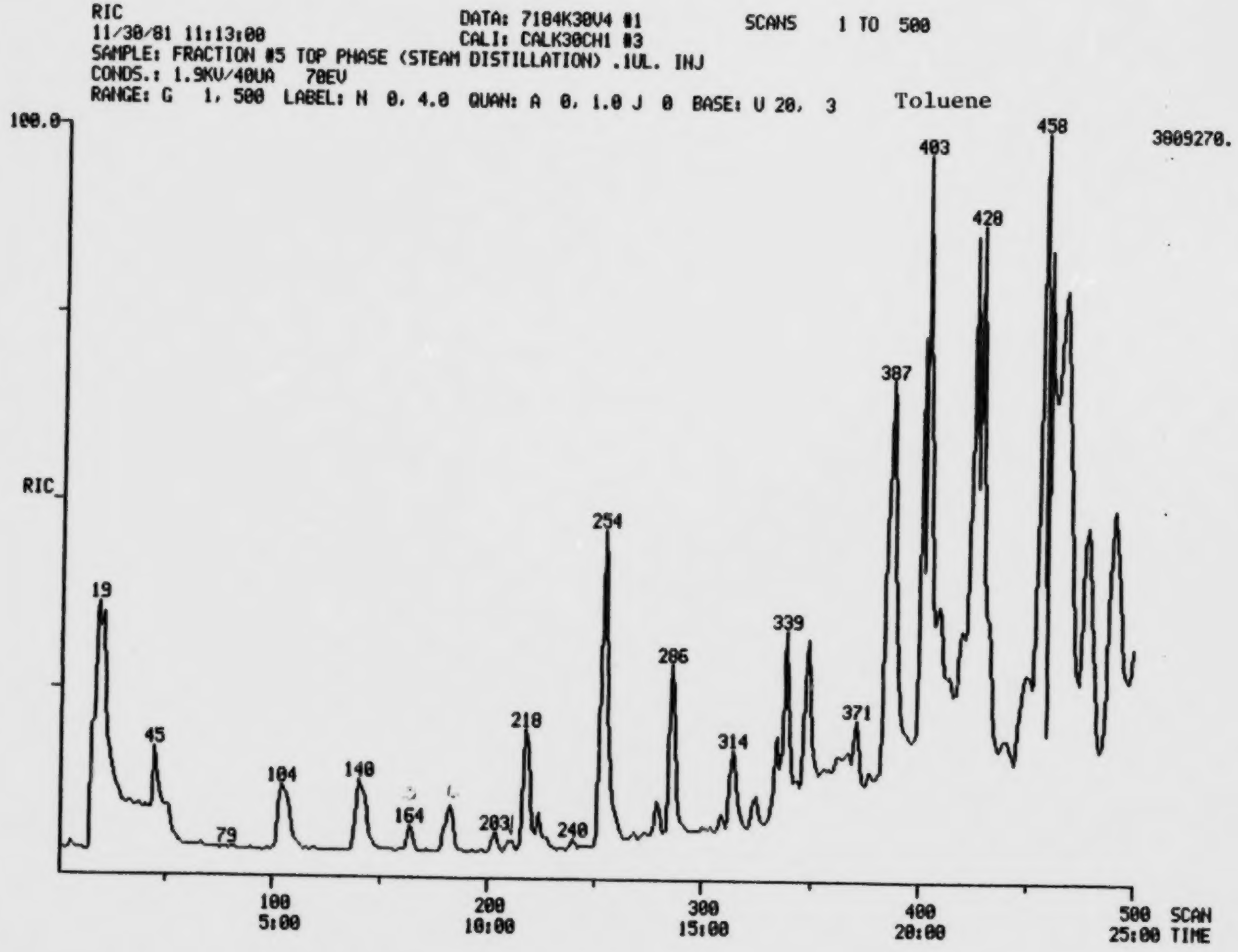

Figure B-4. Total ion chromatogram from on-column injection GC/MS analysis of the top layer of fraction distillation fraction No. 5 for volatiles.

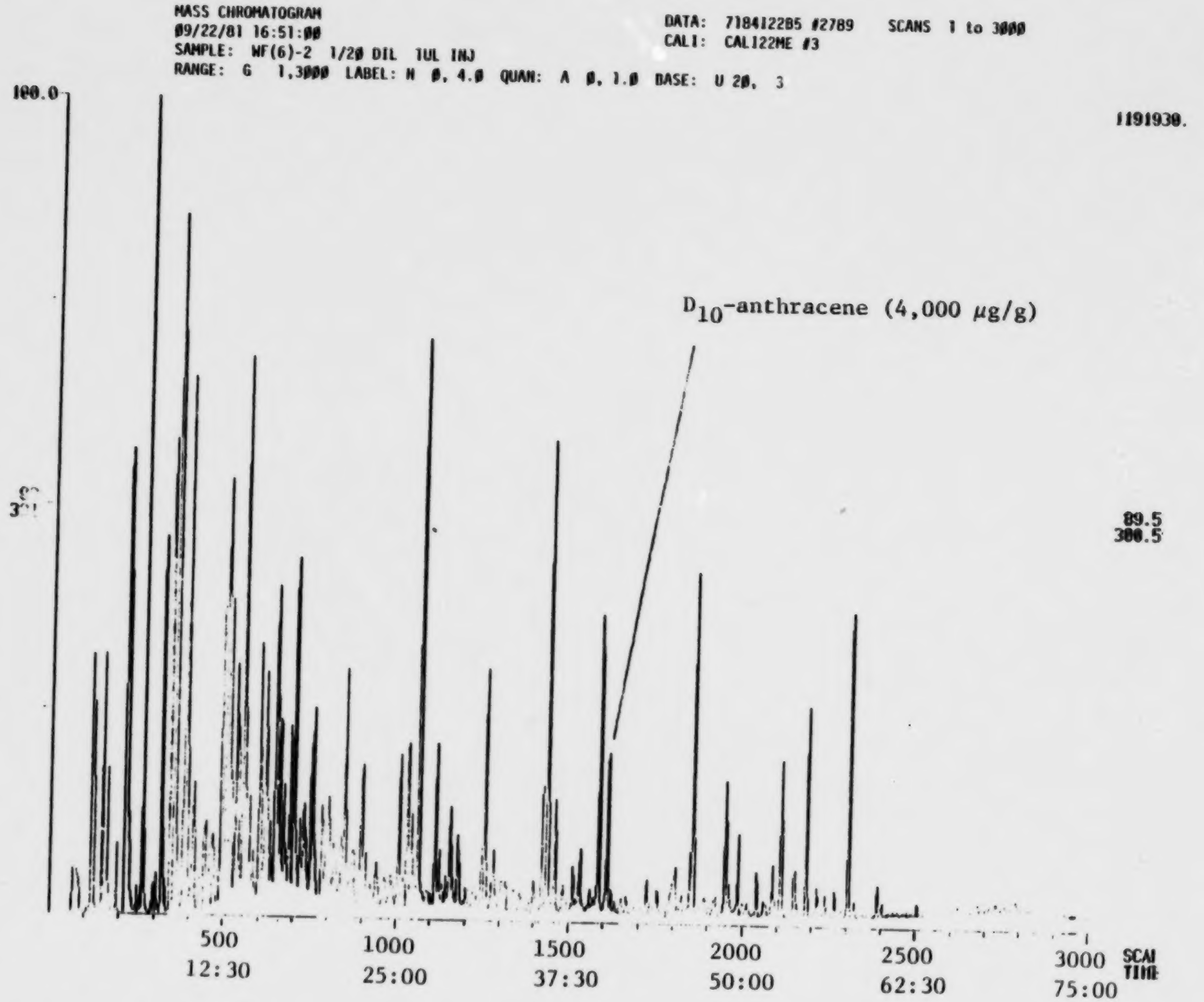

Figure B-5. Total ion chromatogram from GC/MS analysis of homogenized sample WF(6)-2 for semivolatiles.

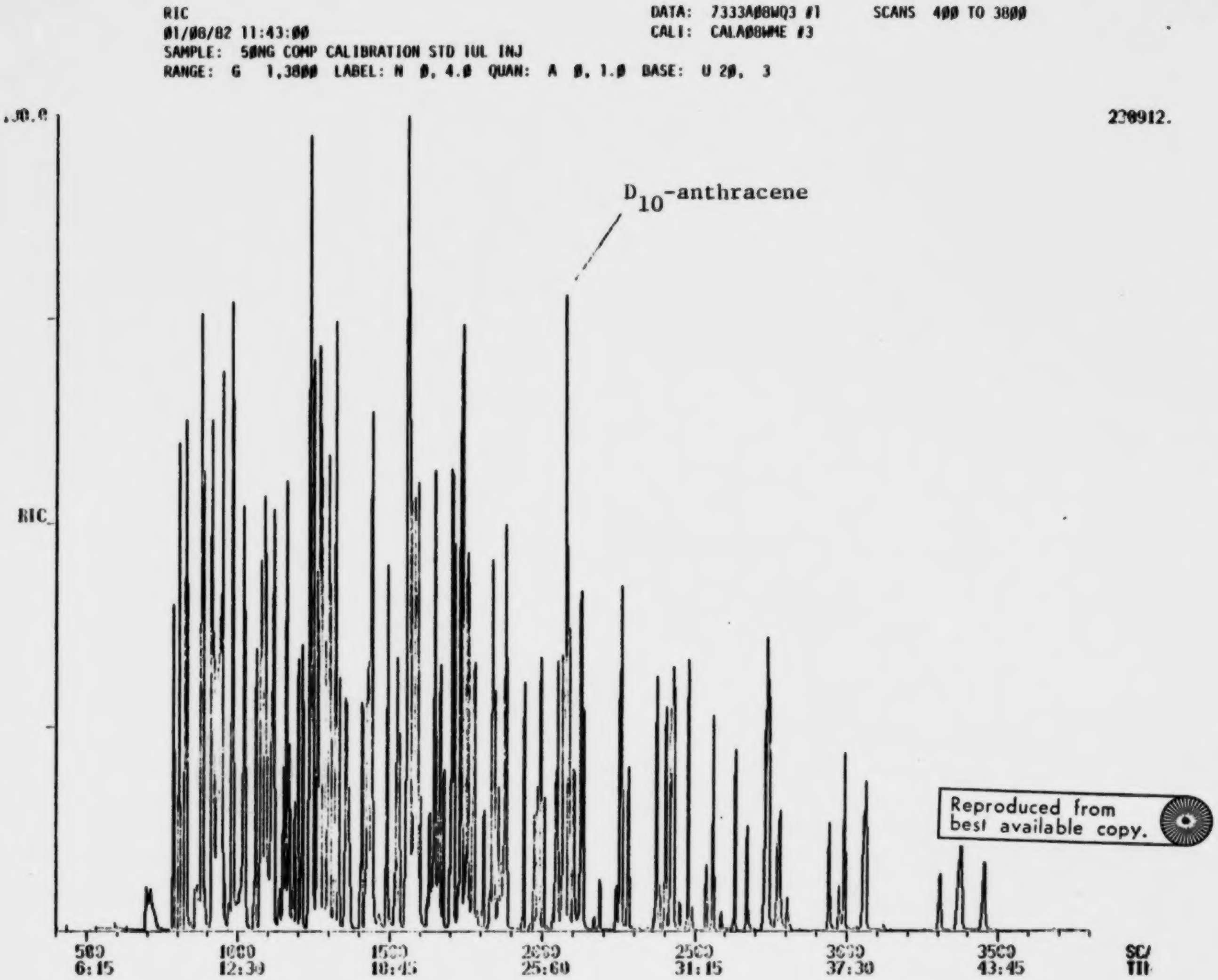

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Figure B-6. Total ion chromatogram from GC/MS analysis of a calibration standard containing 50 ng of about 150 different semivolatile compounds.

APPENDIX C

RESULTS OF ANALYSIS FOR POHCs IN WASTE FEED SAMPLES

Results of analysis for POHCs in waste feed samples are presented in Tables C-1 to C-9 in this appendix.

TABLE C-1. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 1[a]

POHC	Integrated samples (μg/g) 6-hr	Integrated samples (μg/g) 2-hr-A	Integrated samples (μg/g) 2-hr-B	Grab sample (μg/g)[b]
Chloroform	12,000 (7,000)	14,000 (12,000)	5,700 (14,000)	15,000 (15,000)
CCl_4	2,200 (2,000)	2,500 (3,000)	400 (4,000)	3,300 (4,000)
Tetrachloroethylene	2,400 (500)	2,500 (4,000)	2,900 (5,000)	2,600 (5,000)
Hexachloroethane	150 (110)	140 (100)	100 (120)	140 (140)
Hexachlorobenzene	100 (250)	100 (100)	100 (100)	100 (110)
HCCP	4,400 (6,000)	5,600 (6,000)	4,700 (6,000)	3,700 (6,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-A sampling.

TABLE C-2. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 2[a]

POHC	Integrated samples (μg/g) 6-hr	2-hr-A	2-hr-B	Grab sample (μg/g)[b]
Chloroform	7,600 (6,000)	9,800 (12,000)	3,500 (1,200)	8,100 (9,000)
$CC\ell_4$	1,500 (2,000)	3,300 (3,000)	1,100 (-)	1,600 (3,000)
Tetrachloroethylene	3,300 (600)	3,300 (7,000)	1,700 (1,000)	2,200 (5,000)
Hexachloroethane	120 (110)	190 (100)	100 (-)	190 (-)
Hexachlorobenzene	100 (250)	160 (90)	< 100 (< 10)	100 (50)
HCCP	3,700 (3,000)	7,600 (4,000)	690 (1,000)	1,300 (2,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-B sampling.

TABLE C-3. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 3[a]

POHC	Integrated samples (μg/g)			Grab sample (μg/g)[b]
	6-hr	2-hr-A	2-hr-B	
Chloroform	17,200 (9,000)	10,000 (9,000)	15,000 (9,000)	15,000 (14,000)
CCl_4	2,600 (2,000)	1,700 (2,000)	2,100 (1,500)	2,300 (4,000)
Tetrachloroethylene	3,800 (700)	2,100 (4,000)	2,300 (4,000)	2,600 (5,000)
Hexachloroethane	200 (200)	130 (-)	110 (-)	130 (-)
Hexachlorobenzene	260 (400)	100 (60)	100 (70)	100 (60)
HCCP	16,000 (12,000)	2,400 (4,000)	3,200 (3,000)	2,800 (2,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-A sampling.

TABLE C-4. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 4[a]

POHC	Integrated samples (μg/g)			Grab sample (μg/g)[b]
	6-hr	2-hr-A	2-hr-B	
Chloroform	13,200 (5,000)	11,000 (8,000)	14,000 (15,000)	19,000 (16,000)
$CC\ell_4$	1,600 (1,000)	1,200 (1,500)	2,200 (3,000)	2,600 (4,000)
Tetrachloroethylene	2,600 (300)	1,600 (3,000)	2,200 (4,000)	2,900 (6,000)
Hexachloroethane	140 (< 100)	100 (-)	100 (170)	100 (-)
Hexachlorobenzene	< 100 (< 100)	< 100 (< 10)	100 (70)	100 (40)
HCCP	3,100 (700)	90 (800)	650 (4,000)	1,900 (1,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-B sampling.

TABLE C-5. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 5[a]

POHC	Integrated samples (μg/g) 6-hr	2-hr-A	2-hr-B	Grab sample (μg/g)[b]
Chloroform	10,900 (10,000)	21,000 (16,000)	26,000 (22,000)	17,000 (30,000)
CCl_4	1,100 (2,000)	3,300 (3,000)	3,800 (4,000)	5,800 (9,000)
Tetrachloroethylene	2,600 (700)	3,800 (6,000)	4,100 (8,000)	5,300 (11,000)
Hexachloroethane	100 (200)	100 (-)	100 (130)	180 (-)
Hexachlorobenzene	100 (200)	100 (< 10)	100 (80)	100 (70)
HCCP	4,100 (5,000)	4,300 (2,000)	2,500 (4,000)	7,100 (2,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-A sampling.

TABLE C-6. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 6[a]

POHC	Integrated samples (μg/g)			Grab sample (μg/g)[b]
	6-hr	2-hr-A	2-hr-B	
Chloroform	18,000 (10,000)	17,000 (23,000)	10,000 (9,000)	23,000 (40,000)
$CC\ell_4$	2,300 (2,000)	3,000 (5,000)	1,000 (1,300)	5,500 (11,000)
Tetrachloroethylene	3,400 (700)	3,200 (8,000)	1,500 (2,000)	3,900 (13,000)
Hexachloroethane	160 (200)	180 (100)	100 (-)	230 (-)
Hexachlorobenzene	160 (300)	120 (140)	< 100 (110)	140 (110)
HCCP	11,000 (7,000)	12,000 (7,000)	100 (1,000)	8,100 (3,000)

[a] Values in parenthesis are those reported by Rockwell.

[b] Grab sample taken during 2-hr-A sampling.

TABLE C-7. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 7[d]

POHC	Integrated samples (μg/g) 6-hr	2-hr-A	2-hr-B	Grab sample (μg/g)[e]
Trichloroethane[a]	9,600 (40,000)	27,700 (30,000)	27,800 (40,000)	26,600 (30,000)
Tetrachloroethane[b]	1,280 (10,000)	7,000 (8,000)	7,200 (20,000)	6,700 (7,000)
Bromodichloromethane	2,800 (2,000)	2,800 (1,000)	2,900 (1,000)	670 (1,000)
Pentachloroethane	4,200 (16,000)	8,400 (10,000)	7,400 (20,000)	5,900 (30,000)
Hexachloroethane	2,200 (11,000)	7,700 (5,000)	3,600 (12,000)	3,300 (14,000)
Dichlorobenzene[c]	950 (2,000)	1,500 (1,300)	1,100 (2,000)	900 (3,000)

[a] Combined concentrations of 1,1,1-trichloroethane and 1,1,2-trichloroethane, per MRI. Analysis by Rockwell (shown in parenthesis) is only 1,1,1-trichloroethane.

[b] Combined concentrations of 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane. Analysis by Rockwell (shown in parenthesis) is only 1,1,2,2-tetrachloroethane.

[c] Combined concentrations of 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene.

[d] Values in parentheses are those reported by Rockwell.

[e] Grab sample taken during 2-hr-A sampling.

TABLE C-8. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 8[d]

POHC	Integrated samples (μg/g) 6-hr	2-hr-A	2-hr-B	Grab sample (μg/g)[e]
Trichloroethane[a]	31,000 (40,000)	29,000 (30,000)	29,000 (40,000)	28,000 (40,000)
Tetrachloroethane[b]	4,500 (10,000)	8,400 (9,000)	9,100 (10,000)	8,800 (10,000)
Bromodichloromethane	4,200 (2,000)	3,100 (1,000)	1,100 (2,000)	990 (1,000)
Pentachloroethane	2,700 (16,000)	8,300 (30,000)	5,700 (13,000)	8,000 (13,000)
Hexachloroethane	1,400 (6,000)	7,500 (17,000)	5,400 (7,000)	7,300 (6,000)
Dichlorobenzene[c]	500 (1,600)	1,500 (3,000)	1,000 (1,900)	1,500 (1,700)

[a] Combined concentrations of 1,1,1-trichloroethane and 1,1,2-trichloroethane, per MRI. Analysis by Rockwell (shown in parenthesis) is only 1,1,1-trichloroethane.

[b] Combined concentrations of 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane. Analysis by Rockwell (shown in parenthesis) is only 1,1,2,2-tetrachloroethane.

[c] Combined concentrations of 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene.

[d] Values in parentheses are those reported by Rockwell.

[e] Grab sample taken during 2-hr-B sampling.

Note: None of the above POHCs were detected in the fuel oil grab sample taken during Run 8.

TABLE C-9. RESULTS OF ANALYSIS OF POHCs IN WASTE FEED SAMPLES--RUN 9[d]

POHC	Integrated samples (μg/g)			Grab sample(μg/g)[e]
	6-hr	2-hr-A	2-hr-B	
Trichloroethane[a]	31,000 (30,000)	32,000 (30,000)	38,000 (60,000)	36,000 (40,000)
Tetrachloroethane[b]	2,700 (8,000)	8,000 (8,000)	9,800 (14,000)	8,100 (10,000)
Bromodichloromethane	4,000 (17,000)	990 (2,000)	2,800 (2,000)	910 (2,000)
Pentachloroethane	4,200 (17,000)	7,700 (15,000)	8,100 (19,000)	7,400 (18,000)
Hexachloroethane	2,100 (7,000)	3,900 (6,000)	4,700 (7,000)	4,200 (5,000)
Dichlorobenzene[c]	1,100 (2,100)	1,500 (1,800)	1,700 (2,000)	1,600 (1,600)

[a] Combined concentrations of 1,1,1-trichloroethane and 1,1,2-trichloroethane, per MRI. Analysis by Rockwell (shown in parenthesis) is only 1,1,1-trichloroethane.

[b] Combined concentrations of 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane. Analysis by Rockwell (shown in parenthesis) is only 1,1,2,2-tetrachloroethane.

[c] Combined concentrations of 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene.

[d] Values in parentheses are those reported by Rockwell.

[e] Grab sample taken during 2-hr-A sampling.

APPENDIX D

FIGURES SHOWING POHC ANALYSIS RESULTS FOR WASTE FEED SAMPLES

Figures D-1 through D-12 of this appendix display the results of analysis for POHCs in waste feed samples. Analytical results from both MRI and Rockwell International are included in these figures.

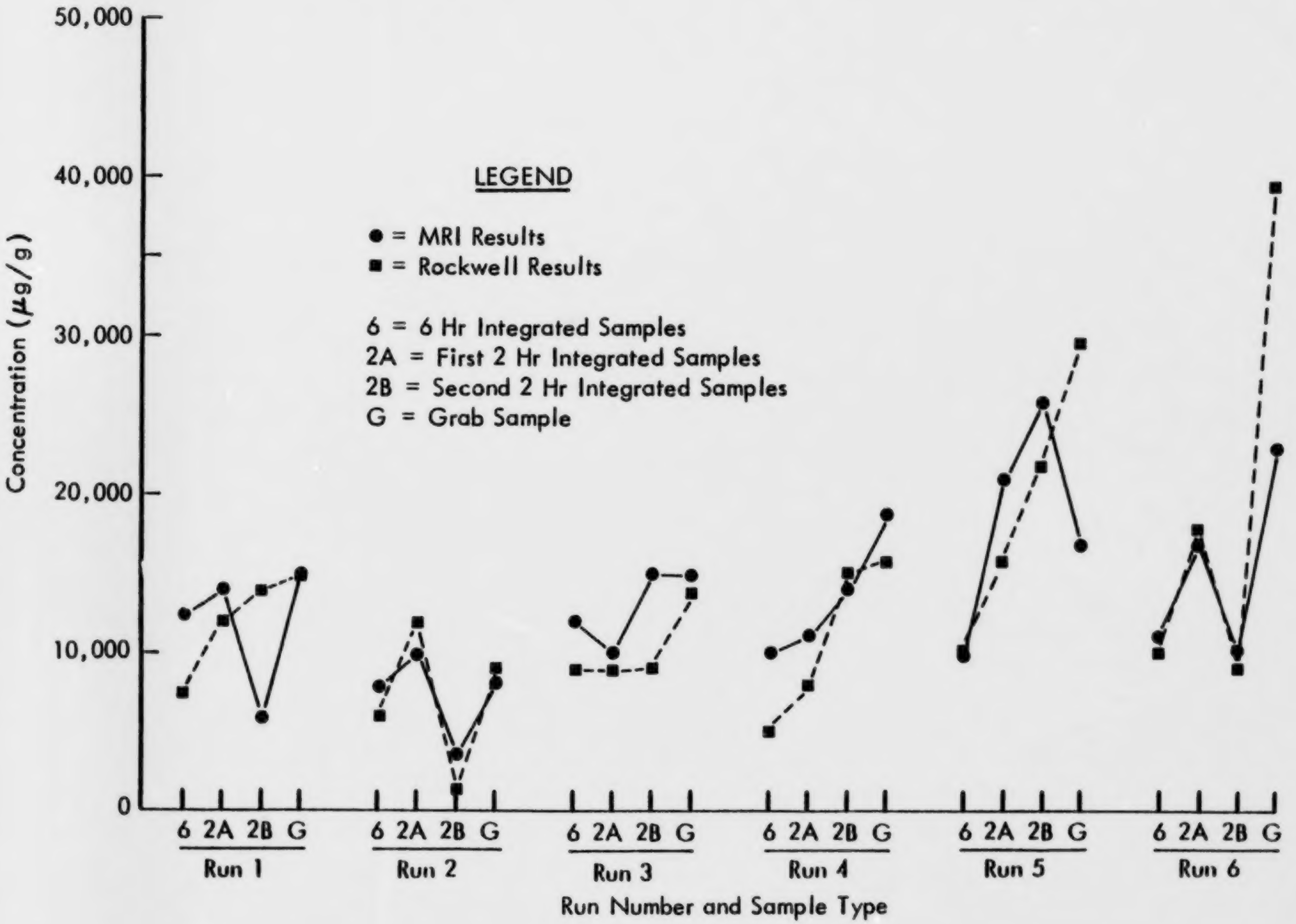

Figure D-1. Results of analysis of chloroform in waste feed samples.

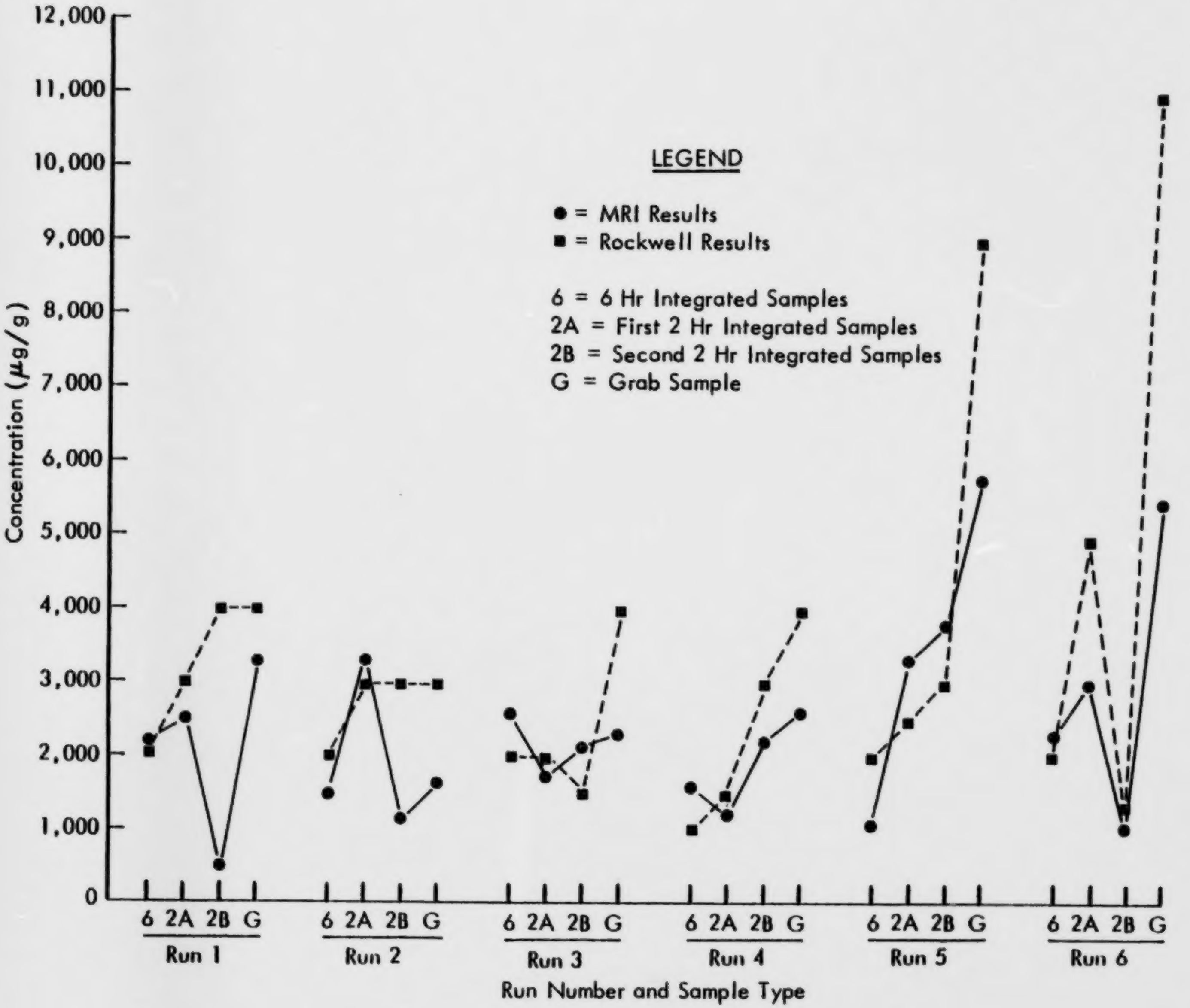

Figure D-2. Results of analysis of carbon tetrachloride in waste feed samples.

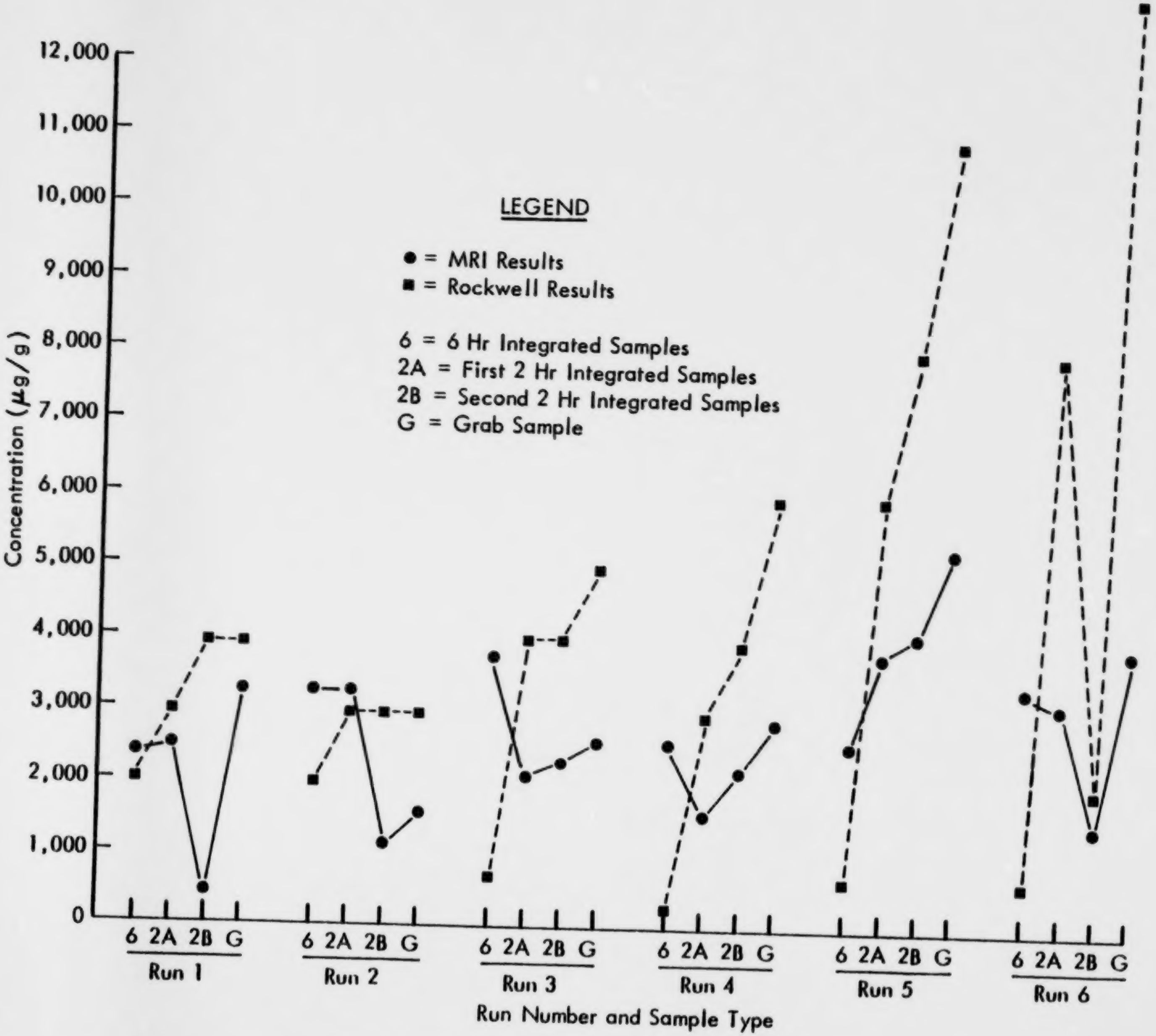

Figure D-3. Results of analysis of tetrachloroethylene in waste feed samples.

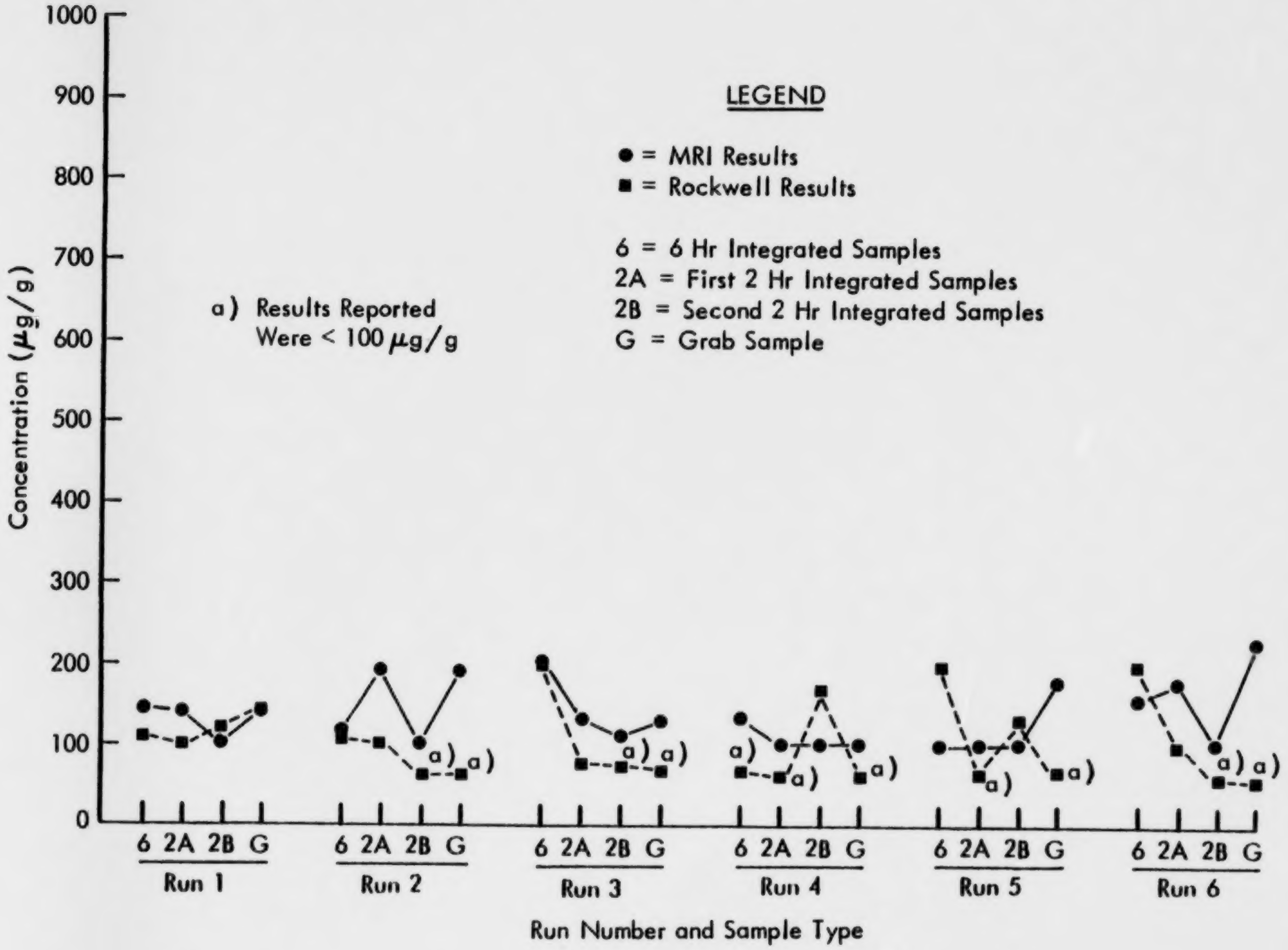

Figure D-4. Results of analysis of hexachloroethane in waste feed samples.

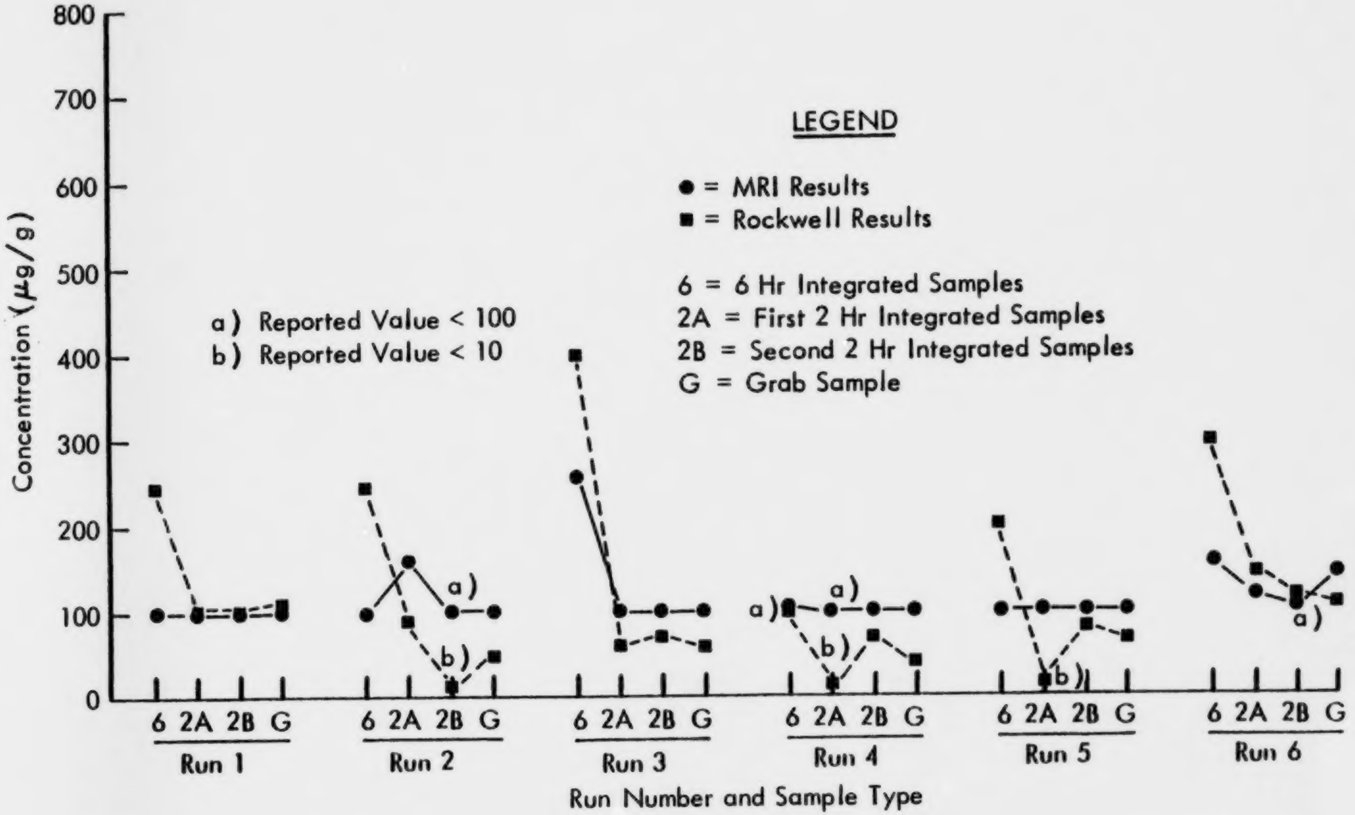

Figure D-5. Results of analysis of hexachlorobenzene in waste feed samples.

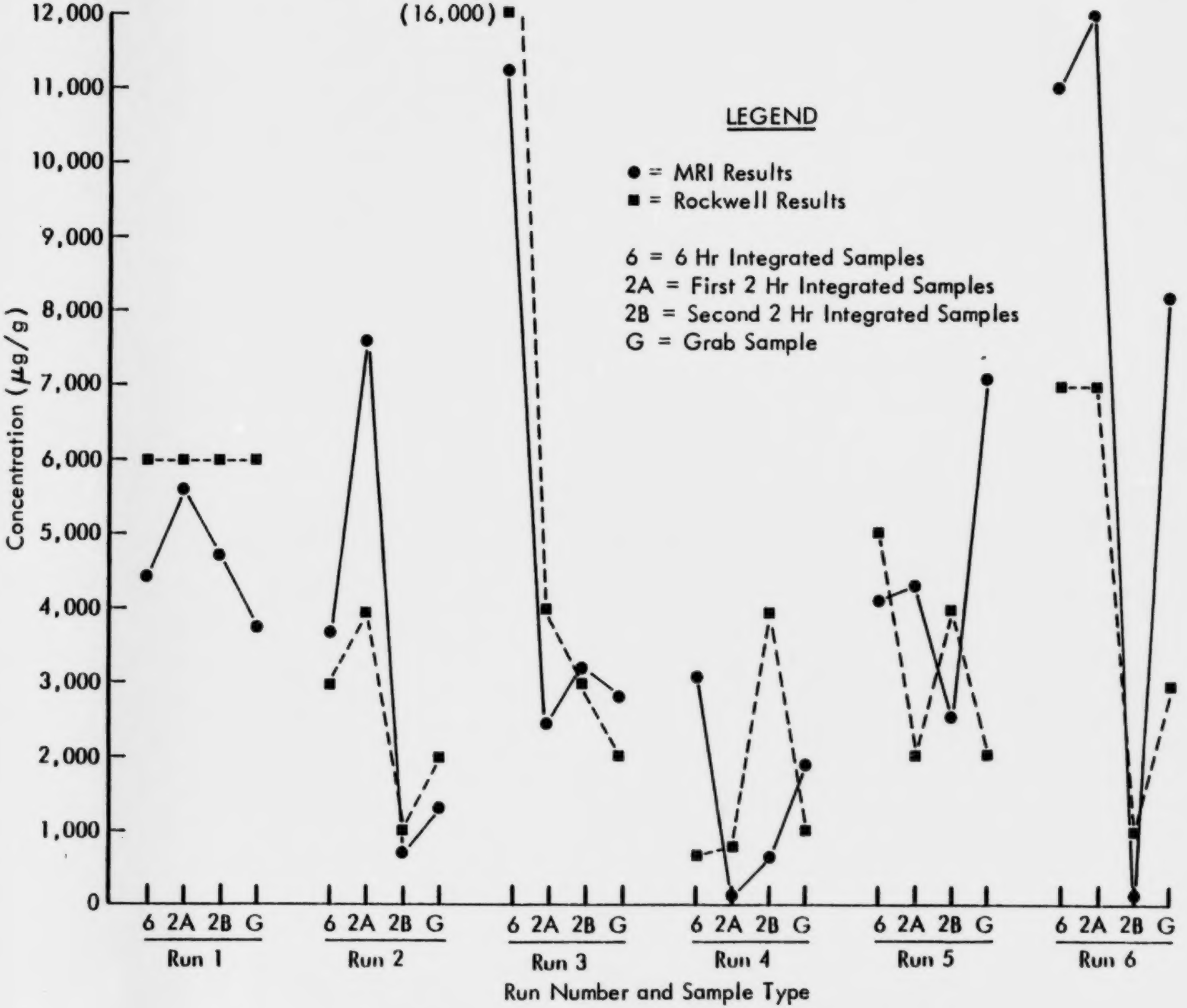

Figure D-6. Results of analysis of HCCP in waste feed samples.

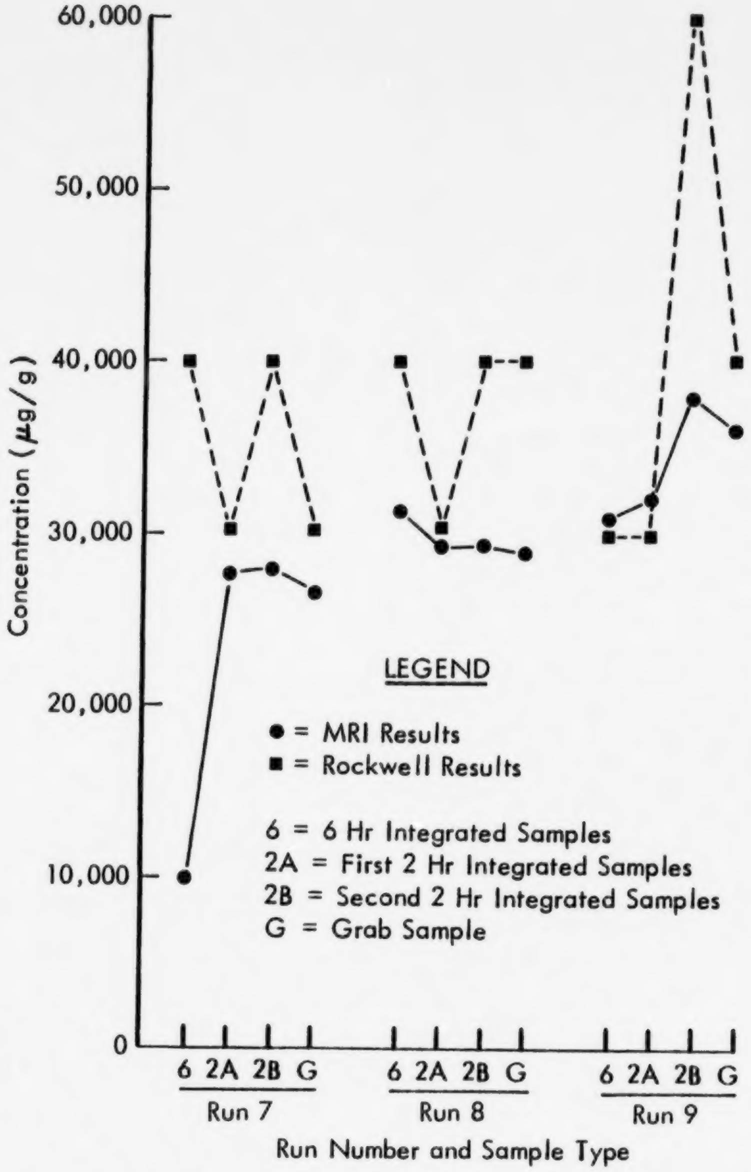

Figure D-7. Results of analysis of trichloroethane in waste feed samples.

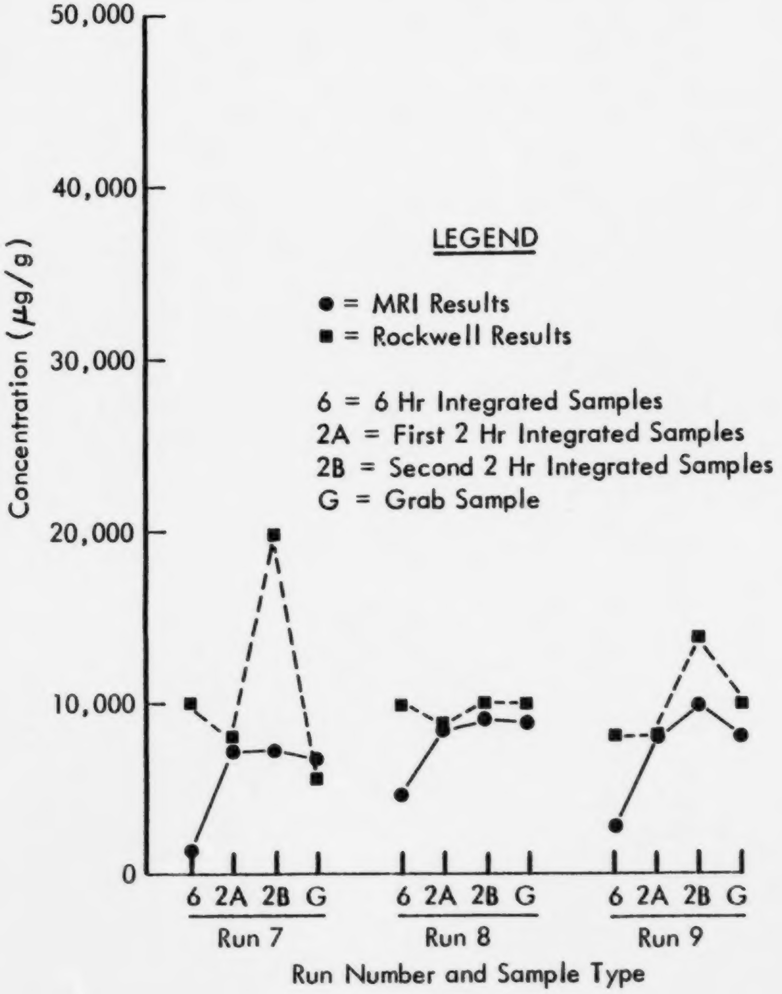

Figure D-8. Results of analysis of tetrachloroethane in waste feed samples.

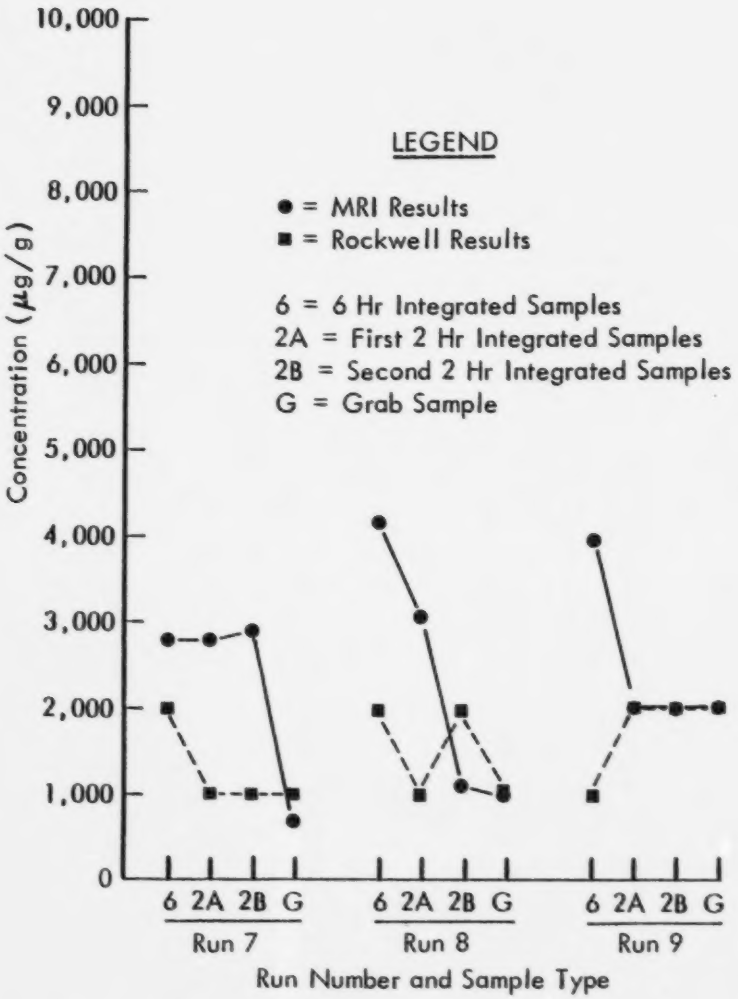

Figure D-9. Results of analysis of bromodichloromethane in waste feed samples.

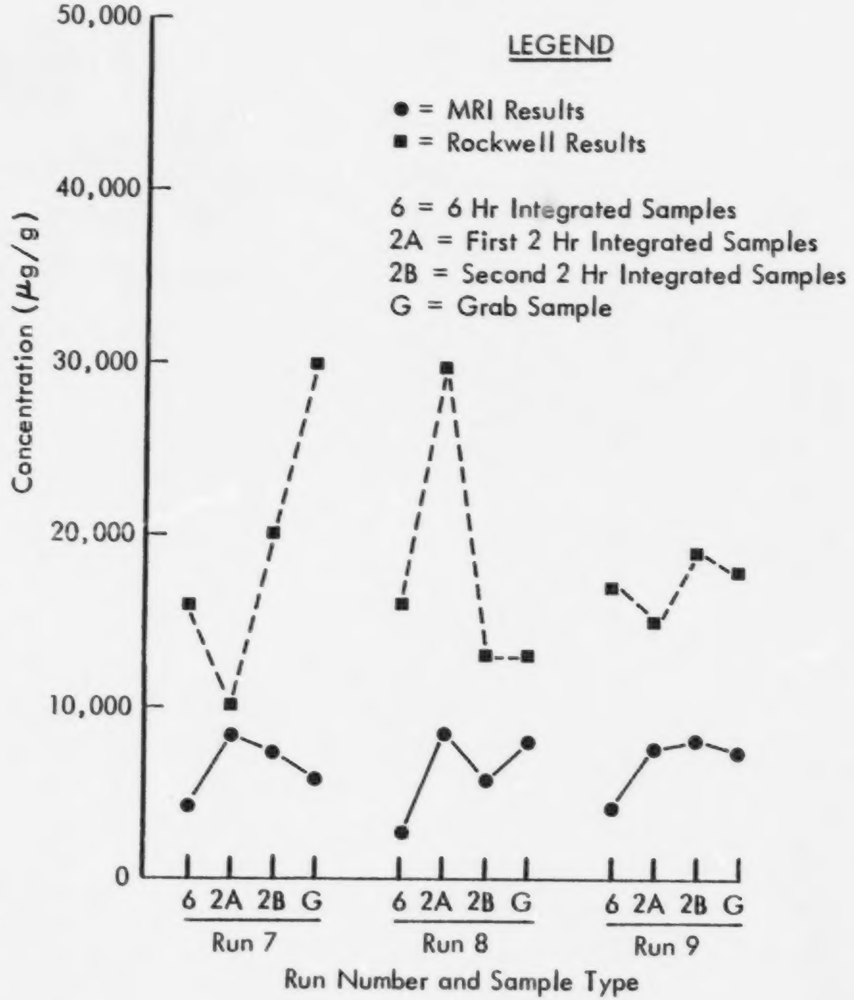

Figure D-10. Results of analysis of pentachloroethane in waste feed samples.

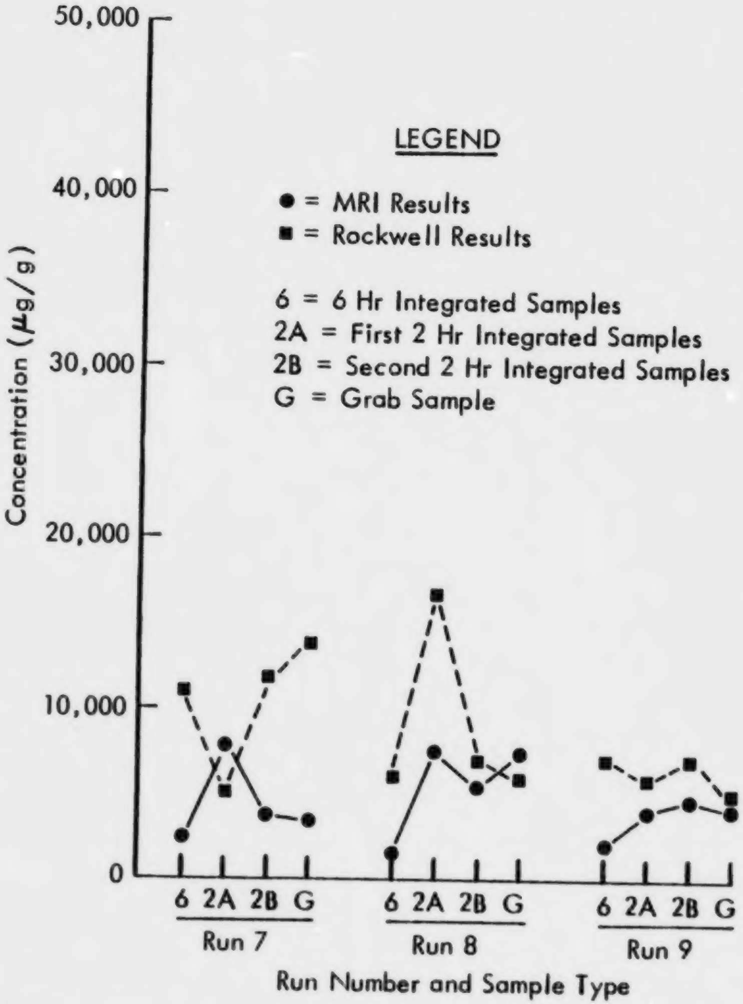

Figure D-11. Results of analysis of hexachloroethane in waste feed samples.

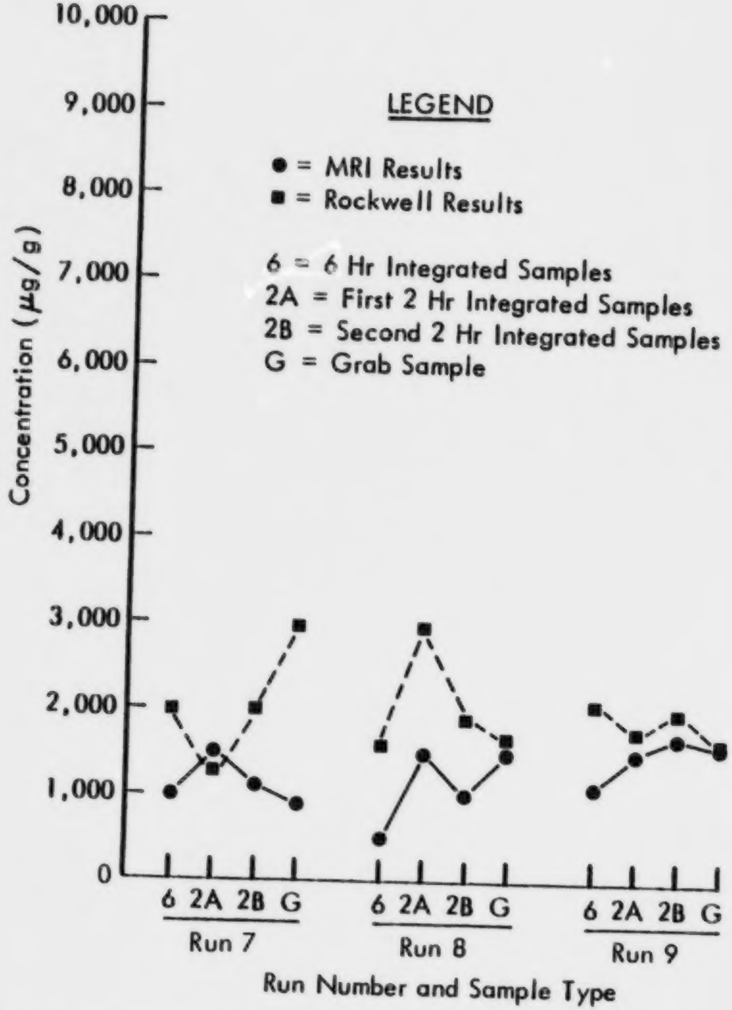

Figure D-12. Results of analysis of dichlorobenzene in waste feed samples.

APPENDIX E

RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES

Results of metals analysis for waste feed samples are summarized in Tables E-1 to E-9 of this appendix.

TABLE E-1. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 1

	Integrated samples (µg/g)				
	6-hr		2-hr-A	2-hr-B	Grab sample (µg/g)
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.004	2.8	< 0.004	0.1	< 0.2
As	4.5	35	6.6	4.1	4.8
Ba	0.4	2,200	1.6	1.0	1.9
Be	< 0.07	< 3	< 0.07	< 0.07	< 0.07
Cd	24	100	19	14	17
Cr	69	2,400	140	74	84
Hg	1.2	14	1.3	1.1	0.9
Ni	16	70	11	6.0	6.0
Pb	550	10,000	580	330	350
Sb	28	230	26	15	16
Se	6.3	30	7.8	1.7	4.7
Tl	1.0	4.4	1.4	1.2	1.6

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-2. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 2

	Integrated samples (μg/g)				Grab sample (μg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	0.2	2.8	0.2	0.08	< 0.019
As	3.0	20	1.9	4.4	4.1
Ba	0.5	3,600	0.6	0.7	1.0
Be	< 0.07	< 0.05	< 0.07	< 0.07	< 0.07
Cd	29	80	11	17	14
Cr	65	2,400	30	77	74
Hg	0.6	15	0.3	0.9	1.1
Ni	15	45	6.9	13	6.0
Pb	630	11,000	240	200	330
Sb	31	420	12	4.2	15
Se	5.5	19	0.5	1.3	1.7
Tl	1.5	3.3	0.7	1.3	1.2

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-3. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 3

	Integrated samples (μg/g)				
	6-hr		2-hr-A	2-hr-B	Grab sample (μg/g)
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.02	1.9	< 0.004	< 0.024	< 0.02
As	6.0	30	6.1	4.2	5.3
Ba	0.7	1,600	1.3	1.0	1.2
Be	< 0.07	0.3	< 0.07	< 0.07	< 0.07
Cd	11	55	16	10	11
Cr	84	2,100	110	77	89
Hg	1.2	13	1.3	0.9	1.1
Ni	8.1	86	10	7.4	7.3
Pb	550	7,900	780	560	580
Sb	18	130	23	15	16
Se	4.4	35	6.5	1.3	3.0
Tl	2.1	30	1.7	1.7	2.0

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-4. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 4

	Integrated samples (μg/g)				Grab sample (μg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.004	2.5	0.2	< 0.019	< 0.07
As	3.5	30	3.6	5.3	4.0
Ba	0.6	1,300	0.8	1.6	0.8
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	28	60	19	17	9
Cr	86	2,400	66	71	45
Hg	1.0	15	0.7	1.0	1.0
Ni	14	140	9.7	6.7	5.0
Pb	920	89,000	670	470	250
Sb	30	270	32	14	10
Se	5.2	45	2.1	3.2	4.0
Tl	1.5	25	1.8	1.7	1.0

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-5. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 5

	Integrated samples (μg/g)				Grab sample (μg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.02	1.2	< 0.02	< 0.02	< 0.004
As	6.5	5.5	9.4	11	14
Ba	0.5	310	1.3	0.4	0.08
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	11	60	7.0	1.4	0.09
Cr	83	2,400	86	73	55
Hg	1.3	4.3	1.8	2.1	2.4
Ni	7.7	110	4.4	1.7	0.8
Pb	390	800	260	12	6.8
Sb	14	70	7.8	4.9	3.6
Se	3.6	30	2.8	3.0	3.7
Tl	2.0	2.3	2.3	2.5	2.1

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-6. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 6

	Integrated samples (µg/g)				Grab sample (µg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.02	1.9	< 0.02	0.05	2.9
As	6.4	27	9.6	4.8	7.9
Ba	0.6	1,200	1.4	1.3	1.3
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	6.5	50	0.4	9.2	0.3
Cr	76	1,900	60	120	50
Hg	1.7	12	1.7	1.1	1.2
Ni	5.0	160	0.6	8.0	0.9
Pb	600	1,700	13	1,300	12
Sb	15	170	2.7	30	1.8
Se	3.2	20	3.7	1.5	5.3
Tl	2.1	25	2.0	2.7	1.7

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-7. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 7

	Integrated samples (μg/g)				Grab sample (μg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.2	< 0.007	< 0.2	< 0.2	< 0.2
As	1.8	< 0.02	6.5	3.7	4.7
Ba	41	1,660	70	93	66
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	2.1	26	2.8	4.3	3.3
Cr	68	1,060	140	150	130
Hg	1.6	8.0	2.5	1.8	2.1
Ni	7.8	74	11	18	13
Pb	260	6,300	430	570	420
Sb	21	120	37	43	37
Se	1.5	< 0.03	3.0	4.6	3.3
Tl	0.8	< 0.04	3.0	2.3	1.8

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-8. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 8

	Integrated samples (μg/g)				Grab sample (μg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.2	< 0.007	0.6	< 0.2	< 0.2
As	5.4	< 0.02	4.9	5.3	3.7
Ba	29	1,100	61	26	16
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	3.1	44	3.7	1.7	1.5
Cr	95	7,000	120	82	61
Hg	1.9	20	1.7	1.6	1.2
Ni	18	120	21	8.6	7.4
Pb	200	20,000	380	160	220
Sb	32	610	37	29	19
Se	3.3	< 0.03	2.9	2.2	2.9
Tl	1.8	25	2.1	1.7	1.0

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

TABLE E-9. RESULTS OF METALS ANALYSIS FOR WASTE FEED SAMPLES--RUN 9

	Integrated samples (µg/g)				Grab sample (µg/g)
	6-hr		2-hr-A	2-hr-B	
Metal	Liquid[a]	Solid[a]	Liquid	Liquid	Liquid
Ag	< 0.02	< 0.007	< 0.2	< 0.2	< 0.2
As	6.8	< 0.02	7.3	6.1	6.0
Ba	4.9	2,500	6.5	4.9	1.7
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07
Cd	0.4	18	0.4	0.4	0.2
Cr	60	1,400	76	66	52
Hg	1.6	11	1.7	1.3	1.2
Ni	3.0	86	2.5	3.4	1.8
Pb	41	7,500	52	46	24
Sb	1.2	260	11	11	7
Se	4.1	< 0.03	3.0	5.0	3.7
Tl	1.1	< 0.04	1.3	1.1	1.0

[a] Ratio of liquid to solid was not determined, but it is estimated that the solid was more than 1% of the sample, but less than 10%.

APPENDIX F

SUMMARY OF MM5 SAMPLING DATA

Test data for Method 5 samplings in this program are tabulated in Tables F-1 to F-9 of this appendix.

TABLE F-1. METHOD 5 TEST DATA--RUN 1

Date	7/21/81			
Run No.	1			
Train ident.	M5(6)-1A	M5(6)-1B	M5(2)-1A	M5(2)-1B
Vol. of gas sampled (Nm^3)	6.243	6.488	2.770	1.619
Sampling time (min)	360	360	126	126
Percent isokinetic	98.7	109.5	109.2	91.6
Moisture content (%)	39	39	40	36
Percent O_2 (dry)	15.6	15.6	15.6	15.6
Percent CO_2 (dry)	4.0	4.0	4.0	4.0
Stack flow rate (act. m^3/min)	1,402	1,478	1,384	1,356
Stack temperature (°C)	89	86	97	95
Stack flow rate (Nm^3/min)	675	717	646	673

TABLE F-2. METHOD 5 TEST DATA--RUN 2

Date	7/23/81			
Run No.	2			
Train ident.	M5(6)-2A	M5(6)-2B	M5(2)-2A	M5(2)-2B
Vol. of gas sampled (Nm^3)	3.707	4.398	1.249	2.241
Sampling time (min)	360	360	126	126
Percent isokinetic	97.1	110.5	106.8	105.2
Moisture content (%)	44.6	45.6	45.3	46.1
Percent O_2 (dry)	10.3	10.3	10.3	10.3
Percent CO_2 (dry)	7.8	7.8	7.8	7.8
Stack flow rate (act. m^3/min)	1,206	1,238	1,050	1,115
Stack temperature (°C)	95	97	99	101
Stack flow rate (Nm^3/min)	525	527	445	465
Particulate weight (grams)				0.4769

TABLE F-3. METHOD 5 TEST DATA--RUN 3

Date	7/24/81			
Run No.	3			
Train ident.	M5(6)-3A	M5(6)-3B	M5(2)-3A	M5(2)-3B
Vol. of gas sampled (Nm^3)	3.917	4.072	1.342	1.331
Sampling time (min)	360	360	126	126
Percent isokinetic	94.7	110.1	104.2	102.8
Moisture content (%)	47.9	53.4	51.2	51.3
Percent O_2 (dry)	8.1	8.1	8.1	8.1
Percent CO_2 (dry)	9.5	9.5	9.5	9.5
Stack flow rate (act. m^3/min)	1,401	1,354	1,287	1,319
Stack temperature (°C)	97	99	97	103
Stack flow rate (Nm^3/min)	569	490	490	493

TABLE F-4. METHOD 5 TEST DATA--RUN 4

Date	7/25/81			
Run No.	4			
Train ident.	M5(6)-4A[a]	M5(6)-4B[a]	M5(2)-4A	M5(2)-4B
Vol. of gas sampled (Nm^3)	5.158	5.322	2.199	2.317
Sampling time (min)	288	287	126	126
Percent isokinetic	82.2	86.6	91.9	85.7
Moisture content (%)	39.8	38.7	42.0	38.8
Percent O_2 (dry)	13.2	13.2	13.2	13.2
Percent CO_2 (dry)	5.8	5.8	5.8	5.8
Stack flow rate (act. m^3/min)	2,252	2,087	1,979	2,126
Stack temperature (°C)	90	89	91	92
Stack flow rate (Nm^3/min)	1,079	1,022	910	1,029

[a] Sampling run was only 80% completed.

TABLE F-5. METHOD 5 TEST DATA--RUN 5

Date	7/26/81			
Run No.	5			
Train ident.	M5(6)-5A	M5(6)-5B	M5(2)-5A	M5(2)-5B
Vol. of gas sampled (Nm^3)	7.272	7.520	2.752	2.611
Sampling time (min)	360	360	126	126
Percent isokinetic	84.7	92.2	96.8	93.8
Moisture content (%)	43.9	45.1	45.7	46.1
Percent O_2 (dry)	12.1	12.1	12.1	12.1
Percent CO_2 (dry)	6.7	6.7	6.7	6.7
Stack flow rate (act. m^3/min)	2,669	2,509	2,548	2,532
Stack temperature (°C)	93	95	96	100
Stack flow rate (Nm^3/min)	1,181	1,080	1,083	1,060
Particulate weight				0.2144

TABLE F-6. METHOD 5 TEST DATA--RUN 6

Date Run No. Train ident.	7/27/81 6 M5(6)-6A	 M5(6)-6B	 M5(2)-6A	 M5(2)-6B
Vol. of gas sampled (Nm^3)	4.646	5.553	2.247	2.448
Sampling time (min)	360	360	126	126
Percent isokinetic	103.6	102.9	97.3	92.3
Moisture content (%)	53.1	50.2	51.6	49.5
Percent O_2 (dry)	11.0	11.0	11.0	11.0
Percent CO_2 (dry)	7.5	7.5	7.5	7.5
Stack flow rate (act. m^3/min)	2,514	2,717	2,348	2,515
Stack temperature (°C)	93	90	102	91
Stack flow rate (Nm^3/min)	935	1,081	879	1,010

TABLE F-7. METHOD 5 TEST DATA--RUN 7

Date	9/30/81			
Run No.	7			
Train ident.	M5(6)-7A	M5(6)-7B	M5(2)-7A	M5(2)-7B
Vol. of gas sampled (Nm^3)	2.885	2.768	1.568	1.679
Sampling time (min)	360	360	126	126
Percent isokinetic	90.1	81.9	89.3	103.0
Moisture content (%)	41.6	37.3	36.5	40.4
Percent O_2 (dry)	12.6	12.6	12.6	12.6
Percent CO_2 (dry)	6.6	6.6	6.6	6.6
Stack flow rate (act. m^3/min)	1,985	1,915	1,885	1,889
Stack temperature (°C)	78	74	74	77
Stack flow rate (Nm^3/min)	954	999	999	927
Particulate weight (grams)	1.924			

TABLE F-8. METHOD 5 TEST DATA--RUN 8

Date	10/1/81			
Run No.	8			
Train ident.	M5(6)-8A	M5(6)-8B	M5(2)-8A	M5(2)-8B
Vol. of gas sampled (Nm^3)	3.607	3.474	1.911	1.698
Sampling time (min)	360	360	126	126
Percent isokinetic	108.1	102.2	110.0	99.8
Moisture content (%)	47.1	46.1	45.5	46.9
Percent O_2 (dry)	12.3	12.3	12.3	12.3
Percent CO_2 (dry)	6.7	6.7	6.7	6.7
Stack flow rate (act. m^3/min)	2,341	2,290	2,225	2,267
Stack temperature (°C)	84	79	79	84
Stack flow rate (Nm^3/min)	995	1,005	988	967
Particulate weight (grams)				1.622

TABLE F-9. METHOD 5 TEST DATA--RUN 9

Date	10/2/81			
Run No.	9			
Train ident.	M5(6)-9A	M5(6)-9B	M5(2)-9A	M5(2)-9B
Vol. of gas sampled (Nm^3)	3.384	3.386	1.775	1.705
Sampling time (min)	360	360	126	126
Percent isokinetic	92.6	81.5	96.3	102.5
Moisture content (%)	49.4	44.6	48.7	52.8
Percent O_2 (dry)	9.7	9.7	9.7	9.7
Percent CO_2 (dry)	8.6	8.6	8.6	8.6
Stack flow rate (act. m^3/min)	2,639	2,700	2,506	2,527
Stack temperature (°C)	81	78	81	90
Stack flow rate (Nm^3/min)	1,089	1,228	1,048	945
Particulate weight (grams)				1.378

APPENDIX G

ANALYSIS RESULTS FOR ALL SAMPLES

Tables G-1 through G-9 list the results of analysis of samples collected on Project No. 7184-G, "Trial Burn Protocol Verification, Performance Evaluation, and Environmental Assessment of the Cincinnati Metropolitan Sewer District Hazardous Waste Incinerator."

The tables designated "A" list the results of analysis for POHCs. The tables designated "B" list the results of analysis for metals. The heading of each column gives the sample identification number. Immediately below the sample identification numbers, the concentration units are given.

In the "A" tables, the results of analysis of volatile POHCs are listed first, semivolatile POHCs next, and PICs last in each column.

Sample identifications consist of a prefix that identifies the type of sample, as shown below, followed by a 6, a 2, or a G in parentheses which identifies it as a 6-hr sample, a 2-hr sample, or a grab sample. The number after the hyphen refers to the run number, with an A or B that differentiates samples taken during the same run.

Sample prefixes:

WF - Waste feed sample
IGS - Integrated gas sample
SST - Stainless steel tank gas sample
M5 - Modified Method 5 sample
SE - Scrubber effluent sample
BA - Bottom ash sample
MW - Makeup water sample
FO - Fuel oil sample

TABLE G-1A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 1

Analyte Concentration units	WF(6)-1[a] (μg/g)	WF(2)-1A[a] (μg/g)	WF(2)-1B[a] (μg/g)	WF(G)-1[a] (μg/g)	IGS-1[b] (μg/m³)	M5(2)-1A[c] (μg)	M5(2)-1B[c] (μg)	M5(6)-1A[c] (μg)	M5(6)-1B[c] (μg)
POHCs									
Chloroform	12,000	14,000	5,700	15,000	6	e	e	e	e
Carbon tetrachloride	2,200	2,500	400	3,300	< 1	e	e	e	e
Tetrachloroethylene	2,400	2,500	2,900	2,600	2	e	e	e	e
Hexachloroethane	150	140[h]	100[h]	140[h]	8	< 1	< 1	< 1	< 1
Hexachlorobenzene	100	100[h]	100[h]	100[h]	8	< 1	< 1	< 1	< 1
Hexachlorocyclopentadiene	4,400	5,600	4,700	3,700	8	< 5	< 5	2	2
PICs									
1 Bromoform	< 200	< 200	< 200	< 200	30	e	e	e	e
2 Dibromochloromethane	< 200	< 200	< 200	< 200	10	e	e	e	e

Analyte Concentration units	M5(Blk)-1[c] Filter (μg)	 Resin (μg)	SE-1[d] (μg/ℓ)	BA-1[d] (μg/ℓ)
POHCs				
Chloroform	e	e	< 1	4
Carbon tetrachloride	e	e	< 1	6
Tetrachloroethylene	e	e	< 1	4
Hexachloroethane	< 1	< 1	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 2.5	< 2.5
Hexachlorocyclopentadiene	< 5	< 5	< 5	< 5
PICs				
1 Bromoform	e	e	< 5	< 5
2 Dibromochloromethane	e	e	< 5	< 5

TABLE G-1B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 1

Analyte	WF(6)-1a		WF(2)-1A[a]	WF(2)-1B[a]	WF(G)-1[a]	M5(2)-1A[c]	M5(2)-1B[c]	M5(6)-1A[c]	M5(6)-1B[c]	M5(Blk)-1[c]
Concentration units	(Liquid) (μg/g)	(Solid)[j] (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(μg)	(μg)	(μg)	(μg)	(μg)
Metals										
Ag	< 0.05 (< 0.7)[f]	2.8 (1.1)[f]	< 0.005	0.1	< 0.1	i	i	i	i	i
As	4.5 (4.2)[f]	36 (18)[f]	6.6	4.1	4.8	< 15	< 0.2	< 1.5	< 7.2	< 1.5
Ba	0.4 (0.7)[f]	2,200 (990)[f]	1.6	1.0	1.9	i	i	i	i	i
Be	< 0.07 (< 0.07)[f]	< 3.0 (< 1.2)[f]	< 0.07	< 0.07	< 0.07	i	i	i	i	i
Cd	24 (14)[f]	100 (40)[f]	19	14	17	i	i	i	i	i
Cr	69 (60)[f]	2,400 (900)[f]	140	74	84	i	i	i	i	i
Hg	1.2 (0.9)[f]	14 (5.4)[f]	1.3	1.1	0.9	< 0.72	0.2	4.1	< 0.7	< 0.2
Ni	16 (6.8)[f]	70 (18)[f]	11	6.0	6.0	i	i	i	i	i
Pb	550 (330)[f]	10,000 (4,000)[f]	580	330	350	i	i	i	i	i
Sb	28 (18)[f]	230 (90)[f]	26	15	16	i	i	i	i	i
Se	6.3 (7.9)[f]	30 (15)[f]	7.8	1.7	4.7	< 9.6	< 1.0	3.6	6.1	< 1.9
Tl	1.0 (1.0)[f]	4.4 (14)[f]	1.4	1.2	1.6	i	i	i	i	i

[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Sample was prepared in duplicate and analyzed.

[g] Semivolatile POHCs not searched for in integrated gas bag samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] These metals not searched for by AAS.

[j] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

TABLE G-2A. RESULTS OF ANALYSIS OF POHCs IN SAMPLES SUBMITTED FROM TEST NO. 2

Analyte Concentration units	WF(6)-2[a] (μg/g)	WF(2)-2A[a] (μg/g)	WF(2)-2B[a] (μg/g)	WF(G)-2[a] (μg/g)	IGS-2[b] (μg/m³)	MS(2)-2A[c] (μg)	MS(2)-2B[c] (μg)	MS(6)-2A[c] (μg)	MS(6)-2B[c] (μg)	FO-2[a,h] (μg/g)
POHCs										
Chloroform	7,600	9,800	3,500	8,100	g	e	e	e	e	< 10
Carbon tetra- chloride	1,500	3,300	1,100	1,600	g	e	e	e	e	< 10
Tetrachloro- ethylene	3,300	3,300	1,700	2,200	g	e	e	e	e	< 10
Hexachloroethane	120	190	100	190	g	< 1 (< 1)[f]	< 1	< 1	< 1	< 100
Hexachlorobenzene	100[j]	160	< 100	100[j]	g	< 1 (< 1)[f]	< 1	< 1	< 1	< 100
Hexachlorocyclo- pentadiene	3,700	7,600	690	1,300	g	< 5 (< 5)[f]	< 5	< 5	< 5	< 100
PICs										
1 Bromoform	< 200	< 200	< 200	< 200	g	e	e	e	e	< 10
2 Dibromochloro- methane	< 200	< 200	< 200	< 200	g	e	e	e	e	< 10

Analyte Concentration units	MS(Blk)-2[c] Filter (μg)	MS(Blk)-2[c] Resin (μg)	SE-2[d] (μg/ℓ)	BA-2[d] (μg/ℓ)	MW-2[d] (μg/ℓ)
POHCs					
Chloroform	e	e	< 1	< 1	< 1
Carbon tetra- chloride	e	e	< 1	< 1	< 1
Tetrachloro- ethylene	e	e	< 1	< 1	< 1
Hexachloroethane	< 1	< 1	< 2.5	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 2.5	< 2.5	< 2.5
Hexachlorocyclo- pentadiene	< 5	< 5	< 5	< 5	< 5
PICs					
1 Bromoform	e	e	< 5	< 5	< 5
2 Dibromochloro- methane	e	e	< 5	< 5	< 5

TABLE G-2B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 2

Analyte Concentration units	WF(6)-2a (Liquid) (µg/g)	WF(6)-2a (Solid)[k] (µg/g)	WF(2)-2A[a] (Liquid) (µg/g)	WF(2)-2B[a] (Liquid) (µg/g)	WF(G)-2[a] (Liquid) (µg/g)	M5(2)-2A[c] (µg)	M5(2)-2B[c] (µg)	M5(6)-2A[c] (µg)	M5(6)-2B[c] (µg)	M5(Blk)-2[c] (µg)
Metals										
Ag	0.2	2.8	0.2	0.08	< 0.02	i	i	i	i	i
As	3.0	20	1.9	4.4	4.8	< 8.2	< 2.0 (< 2.0)[l]	< 0.5	< 0.4	< 4.2
Ba	0.5	3,600	0.6	0.7	1.0	i	i	i	i	i
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07	i	i	i	i	i
Cd	29	80	11	17	18	i	i	i	i	i
Cr	65	2,400	30	77	63	i	i	i	i	i
Hg	0.6	16	0.3	0.9	0.8	0.4	< 0.5 (< 0.5)[l]	< 0.3	< 0.2	0.4
Ni	15	44	6.9	13	11	i	i	i	i	i
Pb	630	11,000	240	200	360	i	i	i	i	i
Sb	31	420	12	4.2	18	i	i	i	i	i
Se	5.5	< 9	0.5	1.3	3.4	< 2.6	< 6.3 (< 6.3)[l]	< 3.3	< 2.6	< 2.7
Tl	1.5	3.3	0.7	1.3	1.6	i	i	i	i	i

[a] Concentrations in waste feeds and fuel oil in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluents, bottom ash , and makeup water in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Results of duplicate analysis of extract.

[g] Gas bag sample lost.

[h] Benzene was detected in the fuel oil at 10 µg/g.

[i] These metals not searched for by AAS.

[j] Compound positively identified from mass spectrum but at a level near the detection limit.

[k] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

[l] Sample was prepared in duplicate and analyzed.

TABLE G-3A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 3

Analyte Concentration units	WF(6)-3[a] (μg/g)	WF(2)-3A[a] (μg/g)	WF(2)-3B[a] (μg/g)	WF(G)-3[a] (μg/g)	IGS-3[b] (μg/m³)	M5(2)-3A[c] (μg)	M5(2)-3B[c] (μg)	M5(6)-3A[c] (μg)	M5(6)-3B[c] (μg)
POHCs									
Chloroform	17,200	10,000	15,000	15,000	7	e	e	e	e
Carbon tetrachloride	2,600	1,700	2,100	2,300	< 1	e	e	e	e
Tetrachloroethylene	3,800	2,100	3,100	2,600	2	e	e	e	e
Hexachloroethane	200	130	110	130	8	< 1 (< 1)[f]	< 1	< 1	< 1 (< 1)[f]
Hexachlorobenzene	260	100[h]	100[h]	100[h]	8	< 1 (< 1)[f]	< 1	< 1	< 1 (< 1)[f]
Hexachlorocyclopentadiene	16,000	2,400	3,200	2,800	8	< 5 (< 5)[f]	< 5	< 5	< 5 (< 5)[f]
PICs									
1 Bromoform	< 200	< 200	< 200	< 200	50	e	e	e	e
2 Dibromochloromethane	< 200	< 200	< 200	< 200	30	e	e	e	e

Analyte Concentration units	M5(Blk)-3[c] Filter (μg)	 Resin (μg)	SE-3[d] (μg/ℓ)	BA-3[d] (μg/ℓ)
POHCs				
Chloroform	e	e	< 1	< 1
Carbon tetrachloride	e	e	< 1	< 1
Tetrachloroethylene	e	e	< 1	< 1
Hexachloroethane	< 1	< 1	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 2.5	< 2.5
Hexachlorocyclopentadiene	< 5	< 5	< 5	< 5
PICs				
1 Bromoform	e	e	< 5	< 5
2 Dibromochloromethane	e	e	< 5	< 5

TABLE G-3B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 3

Analyte	WF(6)-3[a]		WF(2)-3A[a]	WF(2)-3B[a]	WF(G)-3[a]	M5(2)-3A[c]	M5(2)-3B[c]	M5(6)-3A[c]	M5(6)-3B[c]	M5(Blk)-3[c]
Concentration units	(Liquid) (μg/g)	(Solid)[j] (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(μg)	(μg)	(μg)	(μg)	(μg)
Metals										
Ag	< 0.02	1.9	< 0.005	< 0.024	< 0.02 (< 0.07)[k]	i	i	i	i	i
As	6.0	30	6.1	4.2	5.3 (5.0)[k]	< 4.2	< 0.8	< 4.0	< 7.5	< 0.4
Ba	0.7	1,600	1.3	1.0	1.2 (0.7)[k]	i	i	i	i	i
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07 (< 0.07)[k]	i	i	i	i	i
Cd	11	55	16	10	11 (8.2)[k]	i	i	i	i	i
Cr	84	2,100	110	77	89 (67)[k]	i	i	i	i	i
Hg	1.2	13	1.3	0.9	1.1 (1.4)[k]	0.4	0.8	0.4	< 0.4	< 0.2
Ni	8.1	86	10	7.4	7.3 (5.7)[k]	i	i	i	i	i
Pb	550	7,900	780	560	580 (380)[k]	i	i	i	i	i
Sb	18	130	23	15	16 (14)[k]	i	i	i	i	i
Se	4.4	35	6.5	1.3	3.0 (6.4)[k]	< 5.4	< 2.7	< 2.6	< 4.8	< 2.7
Tl	2.1	28	1.7	1.7	2.0 (1.5)[k]	i	i	i	i	i

---

[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Results of duplicate analysis of extract.

[g] Semivolatile POHCs not searched for in integrated gas bag samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] These metals not searched for by AAS.

[j] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

[k] Sample was prepared in duplicate and analyzed.

TABLE G-4A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 4

Analyte Concentration units	WF(6)-4[a] (μg/g)	WF(2)-4A[a] (μg/g)	WF(2)-4B[a] (μg/g)	WF(G)-4[a] (μg/g)	IGS-4[b] (μg/m³)	M5(2)-4A[c] (μg)	M5(2)-4B[c] (μg)	M5(6)-4A[c] (μg)	M5(6)-4B[c] (μg)
POHCs									
Chloroform	13,200	11,000	14,000	19,000	2	e	e	e	e
Carbon tetra-chloride	1,600	1,200	2,200	2,600	< 1	e	e	e	e
Tetrachloro-ethylene	2,600	1,600	2,200	2,900	3	e	e	e	e
Hexachloroethane	140	100[h]	100[h]	100[h]	g	< 1	< 1	< 1	< 1
Hexachlorobenzene	< 100	< 100	100[h]	100[h]	g	< 1	< 1	< 1	< 1
Hexachlorocyclo-pentadiene	3,100	100[h]	650	1,900	g	< 5	< 5	< 5	< 5
PICs									
1 Bromoform	< 200	< 200	< 200	< 200	1	e	e	e	e
2 Dibromochloro-methane	< 200	< 200	< 200	< 200	1	e	e	e	e

Analyte	M5(Blk)-4[c]		SE-4[d]	BA-4[d]
Concentration units	Filter (μg)	Resin (μg)	(μg/ℓ)	(μg/ℓ)
POHCs				
Chloroform	e	e	< 1	4 (6)[f]
Carbon tetra-chloride	e	e	< 1	< 1 (< 1)[f]
Tetrachloro-ethylene	e	e	< 1	2 (2)[f]
Hexachloroethane	< 1	< 1	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 2.5	< 2.5
Hexachlorocyclo-pentadiene	< 5	< 5	< 5	< 5
PICs				
1 Bromoform	e	e	f	f
2 Dibromochloro-methane	e	e	f	f

TABLE G-4B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 4

	WF(6)-4[a]									
Analyte Concentration units	(Liquid) (μg/g)	(Solid)[j] (μg/g)	WF(2)-4A[a] (Liquid) (μg/g)	WF(2)-4B[a] (Liquid) (μg/g)	WF(G)-4[a] (Liquid) (μg/g)	M5(2)-4A[c] (μg)	M5(2)-4B[c] (μg)	M5(6)-4A[c] (μg)	M5(6)-4B[c] (μg)	M5(Blk)-4[c] (μg)
Metals										
Ag	< 0.005	2.5	0.2	< 0.02	< 0.07	i	i	i	i	i
As	3.5	32	3.6	5.3	4.0	< 5.5 (< 1.1)[f]	< 1.4	< 2.0	< 0.8	< 0.4
Ba	0.6	1,300	0.8	1.6	0.8	i	i	i	i	i
Be	0.07	< 0.3	< 0.07	< 0.07	< 0.07	i	i	i	i	i
Cd	28	60	19	17	8.8	i	i	i	i	i
Cr	86	2,400	66	71	45	i	i	i	i	i
Hg	1.0	15	0.7	1.0	1.1	< 0.5 (< 0.5)[f]	0.4	1.2	< 0.07	< 0.2
Ni	14	140	9.7	6.7	5.0	i	i	i	i	i
Pb	920	89,000	670	470	250	i	i	i	i	i
Sb	30	270	22	14	10	i	i	i	i	i
Se	5.2	46	2.1	3.2	4.3	< 7 (< 7.1)[f]	< 2.7	< 2.6	< 1.0	< 2.7
Tl	1.5	27	1.8	1.7	1.2					

[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Samples were prepared in duplicate and analyzed.

[g] Semivolatile POHCs not searched for in integrated gas bag samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] These metals not searched for by AAS.

[j] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

TABLE G-5A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 5

Analyte Concentration units	WF(6)-5[a] (μg/g)	WF(2)-5A[a] (μg/g)	WF(2)-5B[a] (μg/g)	WF(G)-5[a] (μg/g)	IGS-5[b] (μg/m³)	M5(2)-5A[c] (μg)	M5(2)-5B[c] (μg)	M5(6)-5A[c] (μg)
POHCs								
Chloroform	11,900	21,000	26,000	17,000	< 16	e	e	e
Carbon tetra-chloride	1,100	3,300	3,800	5,800	< 80	e	e	e
Tetrachloro-ethylene	2,600	3,800	4,100	5,300	< 30	e	e	e
Hexachloroethane	100[h]	100[h]	100[h]	180	g	< 1	< 1	< 1
Hexachlorobenzene	100[h]	100[h]	100[h]	100[h]	g	< 1	< 1	< 1
Hexachlorocyclo-pentadiene	4,100	4,300	2,500	7,100	g	< 5	< 5	< 5
PICs								
1 Bromoform	< 200	< 200	< 200	< 200	< 60	e	e	e
2 Dibromochloro-methane	< 200	< 200	< 200	< 200	< 60	e	e	e

Analyte	M5(6)-5B[c]				M5(Blk)-5[c]			
Concentration units	Wash (μg)	Filter (μg)	Resin (μg)	Condensate (μg)	Filter (μg)	Resin (μg)	SE-5[d] (μg/ℓ)	BA-5[d] (μg/ℓ)
POHCs								
Chloroform	e	e	e	e	e	e	< 0.1	2
Carbon tetra-chloride	e	e	e	e	e	e	< 0.1	< 0.1
Tetrachloro-ethylene	e	e	e	e	e	e	< 0.1	1
Hexachloroethane	< 1	< 1	< 1	< 1	< 1	< 1	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 1	< 1	< 1	< 1	< 2.5	< 2.5
Hexachlorocyclo-pentadiene	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5
PICs								
1 Bromoform	e	e	e	e	e	e	< 5	< 5
2 Dibromochloro-methane	e	e	e	e	e	e	< 5	< 5

TABLE G-5B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 5

Analyte Concentration units	WF(6)-5[a] (Liquid) (μg/g)	 (Solid)[j] (μg/g)	WF(2)-5A[a] (Liquid) (μg/g)	WF(2)-5B[a] (Liquid) (μg/g)	WF(G)-5[a] (Liquid) (μg/g)	M5(2)-5A[c] (μg)	M5(2)-5B[c] (μg)	M5(6)-5A[c] (μg)	M5(6)-5B[c] (μg)	M5(Blk)-5[c] (μg)
Metals										
Ag	< 0.02	1.2	< 0.02	< 0.02	< 0.005	j	j	j	j	j
As	6.5	5.5	9.4	11	14	< 2.0	< 1.8	< 1.6	< 1.5	< 0.4
Ba	0.5	310	1.3	0.4	0.08	j	j	j	j	j
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07	j	j	j	j	j
Cd	11	20	7.0	1.4	0.09	j	j	j	j	j
Cr	83	420	86	73	55	j	j	j	j	j
Hg	1.3	4.3	1.8	2.1	2.4	< 0.9	< 0.9	< 0.8	< 0.7	< 0.2
Ni	7.7	110	4.4	1.7	0.8	j	j	j	j	j
Pb	390	800	260	13	6.8	j	j	j	j	j
Sb	14	70	7.8	4.9	3.6	j	j	j	j	j
Se	3.6	80	2.8	3.0	3.7	< 13	< 12	< 10	< 9.5	< 2.7
Tl	2.0	2.3	2.3	2.5	2.1	j	j	j	j	j

[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Results of duplicate analysis of extract.

[g] Semivolatile POHCs not searched for in integrated gas bag samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

[j] These metals not searched for by AAS.

TABLE G-6A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 6

Analyte Concentration units	WF(6)-6^a (μg/g)	WF(2)-6A^a (μg/g)	WF(2)-6B^a (μg/g)	WF(G)-6^a (μg/g)	IGS-6^b (μg/m^3)	M5(2)-6A^c (μg)	M5(2)-6B^c (μg)	M5(6)-6A^c (μg)	M5(6)-6B^c (μg)
POHCs									
Chloroform	18,000	17,000	10,000	23,000	< 16	e	e	e	e
Carbon tetra-chloride	2,300	3,000	1,000	5,500	< 80	e	e	e	e
Tetrachloro-ethylene	3,400	3,200	1,500	3,900	< 30	e	e	e	e
Hexachloroethane	160	180	100^h	230	g	< 1	< 1	< 1	< 1
Hexachlorobenzene	160	120	< 100	140	g	< 1	< 1	< 1	< 1
Hexachlorocyclo-pentadiene	11,000	12,000	100^h	8,100	g	< 5	< 5	< 5	< 5
PICs									
1 Bromoform	< 200	< 200	< 200	< 200	< 60	e	e	e	e
2 Dibromochloro-methane	< 200	< 200	< 200	< 200	< 60	e	e	e	e

Analyte Concentration units	M5(Blk)-6^c Filter (μg)	 Resin (μg)	SE-6^d (μg/ℓ)	BA-6^d (μg/ℓ)
POHCs				
Chloroform	e	e	< 1 (< 1)^f	440
Carbon tetra-chloride	e	e	< 1 (< 1)^f	40
Tetrachloro-ethylene	3	3	< 1 (< 1)	40
Hexachloroethane	< 1	< 1	< 2.5	< 2.5
Hexachlorobenzene	< 1	< 1	< 2.5	< 2.5
Hexachlorocyclo-pentadiene	< 5	< 5	< 5	< 5
PICs				
1 Bromoform	e	e	< 5	< 5
2 Dibromochloro-methane	e	e	< 5	< 5

TABLE G-6B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 6

Analyte Concentration units	WF(6)-6[a] (Liquid) (μg/g)	 (Solid)[j] (μg/g)	WF(2)-6A[a] (Liquid) (μg/g)	WF(2)-6B[a] (Liquid) (μg/g)	WF(G)-6[a] (Liquid) (μg/g)	M5(2)-6A[c] (μg)	M5(2)-6B[c] (μg)	M5(6)-6A[c] (μg)	M5(6)-6B[c] (μg)	M5(Blk)-6[c] (μg)
Metals										
Ag	< 0.02	1.9	< 0.02	0.05 (< 0.07)[f]	2.9	i	i	i	i	i
As	6.4	27	9.6	4.8 (5.4)[f]	7.9	< 8.9	< 8.4	< 5.0	< 3.2 (< 3.2)[f]	< 0.4
Ba	0.6	1,200	1.4	1.3 (1.1)[f]	1.3	i	i	i	i	i
Be	< 0.07	< 0.3	< 0.07	< 0.07 (< 0.07)[f]	< 0.07	i	i	i	i	i
Cd	6.5	52	0.4	9.2 (7.9)[f]	0.3	i	i	i	i	i
Cr	76	1,900	60	120 (99)[f]	50	i	i	i	i	i
Hg	1.3	12	1.7	1.1 (1.4)[f]	1.2	< 0.9	0.8	< 0.7	< 0.8 (< 0.8)[f]	0.2
Ni	5.0	160	0.6	8.0 (6.9)[f]	0.9	i	i	i	i	i
Pb	600	1,700	13	1,300 (970)[f]	12	i	i	i	i	i
Sb	15	170	2.7	30 (24)[f]	1.8	i	i	i	i	i
Se	3.2	20	3.7	1.5 (7.5)[f]	5.3	< 12	< 11	< 9.6	< 10 (10)[f]	< 2.7
Tl	2.1	25	2.0	2.7 (2.3)[f]	1.7	i	i	i	i	i

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[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Sample was prepared in duplicate and analyzed.

[g] Semivolatile POHCs not searched for in integrated gas bag samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] These metals not searched for by AAS.

[j] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

TABLE G-7A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 7

Analyte Concentration units	WF(6)-7[a] (μg/g)	WF(2)-7A[a] (μg/g)	WF(2)-7B[a] (μg/g)	WF(G)-7[a] (μg/g)	IGS-7[b] (μg/m³)	SST-7[b] (μg/m³)	MS(2)-7A[c] (μg)	MS(2)-7B[c] (μg)	MS(6)-7A[c] (μg)	MS(6)-7B[c] (μg)
POHCs										
1,1,1-Trichloroethane	8,500	24,000	24,000	23,000	30 (30)[f]	230	e	e	e	e
1,1,2-Trichloroethane	1,100	3,700	3,800	3,600	< 1 (< 1)[f]	< 1	e	e	e	e
1,1,1,2-Tetrachloroethane	650	3,300	3,600	3,100	< 1 (< 1)[f]	< 1	e	e	e	e
1,1,2,2-Tetrachloroethane	630	3,700	3,600	3,600	< 1	< 1	e	e	e	e
Bromodichloromethane	< 800	2,800	2,900	670	45 (48)[f]	37	e	e	e	e
Pentachloroethane	4,200	8,400	7,400	5,900	g	g	< 5	< 5	< 5	< 5
Hexachloroethane	2,200	7,700	3,600	3,300	g	g	< 5	< 5	< 5	< 5
1,2-Dichlorobenzene	850	1,300	960	880	g	g	< 1	< 1	< 1	< 1
1,3-Dichlorobenzene	< 100	100[h]	< 100	< 100	g	g	< 1	< 1	< 1	< 1
1,4-Dichlorobenzene	100[h]	150	110	< 100	g	g	< 5	< 5	< 5	< 5
PICs										
1 Bromoform	< 200	< 200	< 200	< 200	12 (13)[f]	< 1	e	e	e	e
2 Dibromochloromethane	< 200	< 200	< 200	< 200	18 (17)[f]	7	e	e	e	e

Analyte	MS(Blk)-7[c]		SE-7[d]	RA-7[d]
Concentration units	Filter (μg)	Resin (μg)	(μg/ℓ)	(μg/ℓ)
POHCs				
1,1,1-Trichloroethane	e	e	< 1	2
1,1,2-Trichloroethane	e	e	< 1	< 1
1,1,1,2-Tetrachloroethane	e	e	< 1	< 1
1,1,2,2-Tetrachloroethane	e	e	< 1	2
Bromodichloromethane	e	e	< 5	< 5
Pentachloroethane	< 5	< 5	< 2.5	< 2.5
Hexachloroethane	< 5	< 5	< 2.5	< 2.5
1,2-Dichlorobenzene	< 1	< 1	< 2.5	< 2.5
1,3-Dichlorobenzene	< 1	< 1	< 2.5	< 2.5
1,4-Dichlorobenzene	< 1	< 1	< 2.5	< 2.5
PICs				
1 Bromoform	e	e	< 5	< 5
2 Dibromochloromethane	e	e	< 5	< 5

TABLE G-7B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 7

Analyte	WF(6)-7[a]		WF(2)-7A[a]	WF(2)-7B[a]	WF(G)-7[a]					
Concentration units	(Liquid) (μg/g)	(Solid)[h] (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	M5(2)-7A[c] (μg)	M5(2)-7B[c] (μg)	M5(6)-7A[c] (μg)	M5(6)-7B[c] (μg)	M5(Blk)-7[c] (μg)
Metals										
Ag	< 0.2	< 0.007	< 0.2	< 0.2 (< 0.2)[f]	< 0.2	i	i	i	i	i
As	1.8	< 0.02	6.5	3.7 (4.1)[f]	4.7	< 1.2	< 1.3	< 1.4 (< 1.4)[f]	< 1.2	< 1.3
Ba	41	1,700	70	93 (120)[f]	66	i	i	i	i	i
Be	< 0.07	< 0.3	< 0.07	< 0.07 (< 0.07)[f]	< 0.07	i	i	i	i	i
Cd	2.1	26	2.8	4.3 (4.7)[f]	3.3	i	i	i	i	i
Cr	68	1,000	140	150 (170)[f]	130	i	i	i	i	i
Hg	1.6	8.0	2.5	1.8 (2.1)[f]	2.1	0.8	1.2	< 0.1 (< 0.1)[f]	0.4	< 0.1
Ni	7.8	74	11	18 (19)[f]	13	i	i	i	i	i
Pb	260	6,300	430	570 (670)[f]	420	i	i	i	i	i
Sb	21	120	37	43 (40)[f]	37	i	i	i	i	i
Se	1.5	< 0.03	3.0	4.6 (5.9)[f]	3.3	5.7	5.8	< 5.3 (< 5.3)[f]	< 4.8	< 5.0
Tl	0.8	< 0.04	3.0	2.3 (2.6)[f]	1.8	i	i	i	i	i

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[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Sample was prepared in duplicate and analyzed.

[g] Semivolatile POHCs not searched for in integrated gas samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] These metals not searched for by AAS.

[j] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

TABLE G-8A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 8

Analyte Concentration units	WF(6)-8[a] (μg/g)	WF(2)-8A[a] (μg/g)	WF(2)-8B[a] (μg/g)	WF(G)-8[a] (μg/g)	IGS-8[b] (μg/m³)	SST-8[b] (μg/m³)	MS(2)-8A[c] (μg)	MS(2)-8B[c] (μg)	MS(6)-8A[c] (μg)	FO-8[a,g] (μg/g)
POHCs										
1,1,1-Trichloroethane	27,000	27,000	28,000	29,000	j	j	e	e	e	< 10
1,1,2-Trichloroethane	3,900	4,600	5,100	4,800	j	j	e	e	e	< 10
1,1,1,2-Tetrachloroethane	1,700	4,100	4,700	4,300	j	j	e	e	e	< 10
1,1,2,2-Tetrachloroethane	2,300	4,300	4,400	4,500	j	j	e	e	e	< 10
Bromodichloromethane	4,200	3,100	1,100	990	j	j	e	e	e	e
Pentachloroethane	2,700	8,300	5,700	8,000	f	f	< 5	< 5	< 5	< 100
Hexachloroethane	1,400	7,500	5,400	7,300	f	f	< 5	< 5	< 5	< 100
1,2-Dichlorobenzene	510	1,300	960	1,300	f	f	< 1	< 1	< 1	< 100
1,3-Dichlorobenzene	< 100	< 100	< 100	< 100	f	f	< 1	< 1	< 1	< 100
1,4-Dichlorobenzene	< 100	140	100	140	f	f	< 1	< 1	< 1	< 100
PICs										
1 Bromoform	< 200	< 200	< 200	< 200	j	j	e	e	e	< 10
2 Dibromochloromethane	< 200	< 200	< 200	< 200	j	j	e	e	e	< 10

	MS (6)-8B[c]				MS(Blk)-8[c]				
Analyte Concentration units	Wash (μg)	Filter (μg)	Resin (μg)	Condensate (μg)	Filter (μg)	Resin (μg)	SE-8[d] (μg/ℓ)	BA-8[d] (μg/ℓ)	MW-8[d] (μg/ℓ)
POHCs									
1,1,1-Trichloroethane	e	e	e	e	e	e	< 1	< 1	< 1
1,1,2-Trichloroethane	e	e	e	e	e	e	< 1	< 1	< 1
1,1,1,2-Tetrachloroethane	e	e	e	e	e	e	< 1	< 1	< 1
1,1,2,2-Tetrachloroethane	e	e	e	e	e	e	< 1	< 1	2
Bromodichloromethane	e	e	e	e	e	e	< 5	< 5	< 5
Pentachloroethane	< 5						< 2.5	< 2.5	< 2.5
Hexachloroethane	< 5	< 5	< 5	< 5	< 5	< 5	< 2.5	< 2.5	< 2.5
1,2-Dichlorobenzene	< 1	< 1	< 1	< 1	< 1	< 1	< 2.5	< 2.5	< 2.5
1,3-Dichlorobenzene	< 1	< 1	< 1	< 1	< 1	< 1	< 2.5	< 2.5	< 2.5
1,4-Dichlorobenzene	< 1	< 1	< 1	< 1	< 1	< 1	< 2.5	< 2.5	< 2.5
PICs									
1 Bromoform	e	e	e	e	e	e	< 5	< 5	< 5
2 Dibromochloromethane	e	e	e	e	e	e	< 5	< 5	< 5

TABLE G-8B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 8

Analyte Concentration units	WF(6)-8[a] (Liquid) (μg/g)	WF(6)-8[a] (Solid)[i] (μg/g)	WF(2)-8A[a] (Liquid) (μg/g)	WF(2)-8B[a] (Liquid) (μg/g)	WF(G)-8[a] (Liquid) (μg/g)	M5(2)-8A[c] (μg)	M5(2)-8B[c] (μg)	M5(6)-8A[c] (μg)	M5(6)-9B[c] (μg)	M5(Blk)-9[c] (μg)
Metals										
Ag	< 0.2	< 0.007	0.6	< 0.2	< 0.2	k	k	k	k	k
As	5.4	< 0.02	4.9	5.3	3.7	< 1.3	< 2.4	< 1.5 (< 1.5)[h]	< 1.2	< 1.3
Ba	29	1,100	61	26	16	k	k	k	k	k
Be	< 0.07	< 0.3	< 0.07	< 0.07	< 0.07	k	k	k	k	k
Cd	3.1	44	3.7	1.7	1.5	k	k	k	k	k
Cr	95	7,000	120	82	61	k	k	k	k	k
Hg	1.9	20	1.7	1.6	1.2	1.4	< 0.2	< 1.1 (0.9)[h]	1.3	< 0.2
Ni	18	120	21	8.6	7.4	k	k	k	k	k
Pb	200	20,000	380	160	110	k	k	k	k	k
Sb	32	610	37	22	19	k	k	k	k	k
Se	3.3	< 0.03	2.9	2.2	2.9	5.2	11	< 5.9 (< 5.9)[h]	< 2.5	< 5.0
Tl	1.8	25	2.1	1.7	1.0	k	k	k	k	k

[a] Concentrations in waste feeds and fuel oil in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent, bottom ash, and makeup water in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Semivolatile POHCs not searched for in integrated gas bags.

[g] Benzene was detected in fuel oil sample at 10 μg/g.

[h] Sample was prepared in duplicate and analyzed.

[i] The solid material in the waste represented less than 10%, but more than 1% of the waste, by volume.

[j] Gas sample lost.

[k] These metals were not searched for by AAS.

TABLE G-9A. RESULTS OF ANALYSIS OF POHCs AND PICs IN SAMPLES SUBMITTED FROM TEST NO. 9

Analyte Concentration units	WF(6)-9[a] (µg/g)	WF(2)-9A[a] (µg/g)	WF(2)-9B[a] (µg/g)	WF(G)-9[a] (µg/g)	IGS-9[b] (µg/m^3)	SST-9[b] (µg/m^3)	MS(2)-9A[c] (µg)	MS(2)-9B[c] (µg)	MS(6)-9A[c] (µg)	MS(6)-9B[c] (µg)
POHCs										
1,1,1-Trichloro-ethane	27,000	28,000	33,000	32,000	< 1 (< 1)[f]	30	e	e	e	e
1,1,2-Trichloro-ethane	4,000	4,400	4,900	4,400	< 1 (< 1)[f]	< 1	e	e	e	e
1,1,1,2-Tetra-chloroethane	2,100	4,000	4,400	3,700	< 1 (< 1)[f]	< 1	e	e	e	e
1,1,2,2-Tetra-chloroethane	2,400	4,400	5,400	4,400	< 1 (< 1)[f]	< 1	e	e	e	e
Bromodichloro-methane	4,000	900	2,800	910	9 (13)[f]	7	e	e	e	e
Pentachloroethane	4,200	7,700	8,100	7,400	g	g	< 5	< 5	< 5	< 5
Hexachloroethane	2,100	3,900	4,700	4,200	g	g	< 5	< 5	< 5	< 5
1,2-Dichloro-benzene	990	1,400	1,600	1,400	g	g	< 5	< 5	< 5	< 5
1,3-Dichloro-benzene	< 100	< 100	< 100	< 100	g	g	< 5	< 5	< 5	< 5
1,4-Dichloro-benzene	100[h]	140	140	130	g	g	< 5	< 5	< 5	< 5
PICs										
1 Bromoform	< 200	< 200	< 200	< 200	2 (3)[f]	1	e	e	e	e
2 Dibromochloro-methane	< 200	< 200	< 200	< 200	9 (10)[f]	4	e	e	e	e

Analyte	MS(Blk)-9[c]			
Concentration units	Filter (µg/g)	Resin (µg)	SE-9[d] (µg/ℓ)	BA-9[d] (µg/ℓ)
POHCs				
1,1,1-Trichloro-ethane	e	e	< 0.1	< 0.1
1,1,2-Trichloro-ethane	e	e	< 0.1	< 0.1
1,1,1,2-Tetra-chloroethane	e	e	< 0.1	< 0.1
1,1,2,2-Tetra-chloroethane	e	e	< 0.1	< 0.1
Bromodichloro-methane	e	e	< 5	< 5
Pentachloroethane	< 5	< 5	< 2.5	< 2.5
Hexachloroethane	< 5	< 5	< 2.5	< 2.5
1,2-Dichloro-benzene	< 1	< 1	< 2.5	< 2.5
1,3-Dichloro-benzene	< 1	< 1	< 2.5	< 2.5
1,4-Dichloro-benzene	< 1	< 1	< 2.5	< 2.5
PICs				
1 Bromoform	e	e	< 5	< 5
2 Dibromochloro-methane	e	e	< 5	< 5

TABLE G-9B. RESULTS OF ANALYSIS OF METALS IN SAMPLES SUBMITTED FROM TEST NO. 9

Analyte Concentration units	WF(6)-9[a]		WF(2)-9A[a]	WF(2)-9B[a]	WF(G)-9[a]	M5(2)-9A[c]	M5(2)-9B[c]	M5(6)-9A[c]	M5(6)-9B[c]	M5(Blk)-9[c]
	(Liquid) (μg/g)	(Solid)[i] (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(Liquid) (μg/g)	(μg)	(μg)	(μg)	(μg)	(μg)
Metals										
Ag	< 0.02	< 0.007 (< 0.007)[f]	< 0.2	< 0.2	< 0.2	j	j	j	j	j
As	6.8	< 0.02 (< 0.02)[f]	7.3	6.1	6.0	< 1.3	< 1.3	< 1.6	< 0.7	< 1.3
Ba	4.9	2,500 (3,400)[f]	6.5	4.9	1.7	j	j	j	j	j
Be	< 0.07	< 0.3 (< 0.3)[f]	< 0.07	< 0.07	< 0.07	j	j	j	j	j
Cd	0.4	18 (19)[f]	0.4	0.4	0.2	j	j	j	j	j
Cr	60	1,400 (2,100)[f]	76	66	52	j	j	j	j	j
Hg	1.6	11 (14)[f]	1.7	1.3	1.2	0.2	0.4	0.6	0.3	< 0.1
Ni	3.0	86 (83)[f]	2.5	3.4	1.8	j	j	j	j	j
Pb	41	7,500 (9,900)[f]	52	46	24	j	j	j	j	j
Sb	9.2	260 (200)[f]	11	11	7	j	j	j	j	j
Se	4.1	< 0.03 (< 0.03)[f]	3.0	5.0	3.7	5.2	5.7	< 4.8	< 2.5	< 5.0
Tl	1.1	< 0.04 (< 0.04)[f]	1.3	1.1	1.0	j	j	j	j	j

[a] Concentrations in waste feeds in micrograms per gram (parts per million).

[b] Concentrations in integrated gas bags in nanograms per liter (micrograms per cubic meter).

[c] Concentrations in modified Method 5 trains in total micrograms.

[d] Concentrations in scrubber effluent and bottom ash in micrograms per liter.

[e] Volatile compounds which could not be identified in Method 5 train extracts.

[f] Sample was prepared in duplicate and analyzed.

[g] Semivolatile POHCs not searched for in integrated gas samples.

[h] Compound positively identified from mass spectrum but at a level near the detection limit.

[i] The solid material in the waste represented less than 10%, but more than 1% of the total waste, by volume.

[j] These metals not searched for by AAS.

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APPENDIX H

SUMMARY OF DRE CALCULATION RESULTS

Results of DRE calculation for various test runs are summarized in Tables H-1 to H-9 of this appendix.

TABLE H-1. SUMMARY OF DRE CALCULATION RESULTS--RUN 1

POHC	Volatiles by integrated gas bag
Chloroform	99.998
Carbon tetrachloride	> 99.995
Tetrachloroethylene	99.999

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.998	> 99.998	> 99.996	> 99.99
Hexachlorobenzene	> 99.997	> 99.997	> 99.993	> 99.99
Hexachlorocyclopentadiene	99.9999	99.9999	> 99.9994	> 99.999

TABLE H-2. SUMMARY OF DRE CALCULATION RESULTS--RUN 2

POHC	Volatiles by integrated gas bag			
Chloroform	No analysis Gas bag was flat			
Carbon tetrachloride				
Tetrachloroethylene				
	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.998	> 99.998	> 99.993	> 99.995
Hexachlorobenzene	> 99.997	> 99.997	> 99.992	ND[a]
Hexachlorocyclopentadiene	99.9998	99.99992	> 99.9992	> 99.996

[a] Not determinable because both input and outputs were "less than" values.

TABLE H-3. SUMMARY OF DRE CALCULATION RESULTS--RUN 3

POHC	Volatiles by integrated gas bag
Chloroform	99.9995
Carbon tetrachloride	> 99.9993
Tetrachloroethylene	99.999

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.999	> 99.999	> 99.992	> 99.99
Hexachlorobenzene	> 99.999	> 99.999	> 99.999	> 99.99
Hexachlorocyclopentadiene	99.99998	99.99998	> 99.998	> 99.998

TABLE H-4. SUMMARY OF DRE CALCULATION RESULTS--RUN 4

POHC	Volatiles by integrated gas bag
Chloroform	99.9997
Carbon tetrachloride	> 99.999
Tetrachloroethylene	99.997

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.997	> 99.997	> 99.992	> 99.993
Hexachlorobenzene	ND[a]	ND[a]	ND[a]	> 99.993
Hexachlorocyclopentadiene	> 99.9994	> 99.9994	> 99.96[b]	> 99.995

[a] Not determinable because both input and output were "less than" values.

[b] It was not possible to determine if DRE of 99.99% was achieved in this case because concentration of HCCP for this waste sample was quite low (90 ppm) and detection limit for HCCP is higher than for other POHCs (5 μg).

TABLE H-5. SUMMARY OF DRE CALCULATION RESULTS--RUN 5

POHC	Volatiles by integrated gas bag
Chloroform	> 99.9989
Carbon tetrachloride	> 99.96[a]
Tetrachloroethylene	> 99.99

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.996	> 99.99	> 99.992	> 99.993
Hexachlorobenzene	> 99.996	> 99.99	> 99.992	> 99.993
Hexachlorocyclopentadiene	> 99.9996	> 99.999	> 99.999	> 99.999

[a] Detection limits were high because inadequate sample was available for analysis from the gas bag. Therefore, the DRE could only be expressed as > 99.96%.

TABLE H-6. SUMMARY OF DRE CALCULATION RESULTS--RUN 6

POHC	Volatiles by integrated gas bag
Chloroform	> 99.998
Carbon tetrachloride	> 99.9[a]
Tetrachloroethylene	> 99.97[a]

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Hexachloroethane	> 99.998	> 99.995	> 99.995	> 99.994
Hexachlorobenzene	> 99.998	> 99.995	> 99.993	> 99.994
Hexachlorocyclopentadiene	> 99.9998	> 99.9997	> 99.9996	> 99.97[b]

[a] Detection limits were high because inadequate sample was available for analysis from the gas bag. Therefore, the DREs could only be expressed as > 99.9% or > 99.97%.

[b] It was not possible to determine if DRE of 99.99% was achieved in this case because concentration of HCCP for this waste sample was quite low (100 ppm) and detection limit for HCCP is higher than for other POHCs (5 μg).

TABLE H-7. SUMMARY OF DRE CALCULATION RESULTS--RUN 7

POHC	Volatiles	
	Integrated gas bag	Stainless steel tank
Trichloroethane	99.998	99.985
Tetrachloroethane	> 99.9997	> 99.9997
Bromodichloromethane	99.97	99.976

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Pentachloroethane	> 99.9999	> 99.9998	> 99.9999	> 99.9998
Hexachloroethane	> 99.9997	> 99.9996	> 99.9998	> 99.9997
Dichlorobenzene	> 99.998	> 99.998	> 99.997	> 99.996

TABLE H-8. SUMMARY OF DRE CALCULATION RESULTS--RUN 8

POHC	Integrated gas bag	Stainless steel tank
Trichloroethane	No analysis Gas bag was flat	Sample lost due to instrument problems (GC/MS)
Tetrachloroethane		
Bromodichloromethane		

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Pentachloroethane	> 99.9998	> 99.9994	> 99.9999	> 99.9998
Hexachloroethane	> 99.9996	> 99.999	> 99.9999	> 99.9998
Dichlorobenzene	> 99.997	> 99.99	> 99.998	> 99.997

TABLE H-9. SUMMARY OF DRE CALCULATION RESULTS--RUN 9

POHC	Volatiles Integrated gas bag	Volatiles Stainless steel tank
Trichloroethane	> 99.99996	99.999
Tetrachloroethane	> 99.9998	> 99.9998
Bromodichloromethane	99.995	99.996

	Semivolatiles by modified Method 5 train			
	6-hr trains		2-hr trains	
	A	B	A	B
Pentachloroethane	> 99.9999	> 99.9998	> 99.9999	> 99.9999
Hexachloroethane	> 99.9998	> 99.9997	> 99.9997	> 99.9998
Dichlorobenzene	> 99.999	> 99.999	> 99.998	> 99.998

APPENDIX I

REPORT ON QUALITY ASSURANCE TESTS

FIELD AND LABORATORY QUALITY ASSURANCE AUDITS FOR TRIAL BURN PROTOCOL EVALUATION: TEST II

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SECTION I-1

INTRODUCTION

The MSD incinerator project (MRI Project No. 7184-G) was conducted to evaluate a trial burn protocol, to evaluate performance, and to obtain environmental assessment information on the Cincinnati Metropolitan Sewer District hazardous waste incinerator. The project was done in two distinct tests. The tests were to examine POHC emission and other performance factors using waste feeds of differing composition.

Each test was conducted in two parts--Field Sampling and Laboratory Analysis. Field sampling included:

- Waste feed
- Bottom ash
- Scrubber effluent
- Stack effluent

Laboratory analysis consisted of analyzing the field samples by:

- Atomic absorption spectroscopy (trace metals)
- Inductively coupled emission spectroscopy (trace metals)
- GC/MS
- Titrametric analysis or technicon autoanalyzer (chlorides)

Independent quality assurance (QA) activities were carried out during Test II only. The QA activities were designed to examine and document performance and procedural aspects of field and laboratory work by using performance and systems audits. This report presents the findings of the audits.

SECTION I-2

AUDIT METHODOLOGY

Performance and systems audits were carried out for both field sampling and laboratory analysis. Performance audits were intended to measure the accuracy and precision of reported numerical values against known values. Systems audits are intended to determine adherence to protocol, procedures, and accepted laboratory practices.

FIELD AUDIT PROCEDURE

The purpose of the field audit was to determine the overall performance of field sampling equipment against standard measurements and to examine adherence to field protocol and procedures. Overall, both audits combined assist in ensuring that the samples are representative.

Field Performance Audit

All equipment used in the conduct of the field performance audit was calibrated prior to departure. All gases used as performance standards were Scott standard gases of known composition. All field performance audits were conducted on site during actual operation of the equipment.

Field Systems Audit

The intent of the systems audit was to look at all aspects of equipment configuration, data recording, protocol availability, personnel qualification, equipment calibration and maintenance, etc.

A field systems audit form was prepared prior to departure. A blank copy of the systems audit form is included as Attachment I. Procedural aspects during the three phases of sampling (pre-sampling, sampling, and post-sampling) were examined. The auditor actually witnessed the three phases and checked the appropriate column "yes," "no," or "N/A" (not applicable). Comments were entered as necessary.

The field systems audit specifically inspected:

- Modified Method 5 sampling
- Process data recording

* Integrated bag sampling

* Stack velocity measurements

* Chloride sampling

* Scrubber effluent sampling

* Waste feed sampling

* Continuous gas analyzers

LABORATORY AUDIT PROCEDURE

The laboratory audit had two purposes: one, to assess the interlaboratory analytical performance of MRI and Rockwell chemists; and the other, to examine analytical performance and procedural aspects of laboratory work conducted at MRI.

Interlaboratory Performance Audit

The objective of this part of the laboratory audit was to prepare and submit performance audit samples which would determine the degree of comparability of results from MRI and Rockwell.

Two sample sets consisting of 12 organic chemicals of known amounts were prepared in acetone. Each sample set was subdivided into six clean ampoules which were subsequently sealed and randomly numbered. Three ampoules from each set were given to Rockwell and MRI for analysis in duplicate.

MRI Performance Audit

MRI performance audit samples were prepared for chloride, POHC, and trace metals analysis.

Chloride performance audit samples were prepared by adding the appropriate amount of sodium chloride to 0.1 $\underline{N}$ sodium hydroxide. Aliquots of 15 ml were dispensed into clean polyethylene sample bottles. The bottles were randomly numbered and given to the chemist during the conduct of the sample analysis.

Two samples containing POHCs were prepared in acetone. Each sample was subdivided into ampoules which were sealed and randomly numbered. The ampoules were given to MRI analysts for triplicate analysis.

Arsenic, selenium, and mercury were added to ammonium persulfate in clean polyethylene sample bottles. These bottles were randomly numbered and given to the chemist for analysis.

MRI Systems Audit

The purpose of the laboratory systems audit was the examination of the procedural aspects of laboratory operations as opposed to the determination of actual numerical values by analysis.

The systems audit looked at:

- Waste feed sample preparation for trace metals analysis
- ICP analysis of waste feed
- Extraction and compositing of Modified Method 5 sample trains.
- Volatile organics analysis by GC/MS

The form used to assess these procedural aspects is shown in Attachment II.

SECTION I-3

RESULTS

FIELD AUDIT

Field Performance Audit

Table I-1 summarizes the findings of the field performance audit conducted on the Method 5 meter boxes. The audit device was a critical orifice calibrated by the U.S. EPA. The relative percent accuracy was calculated as follows:

$$\% A = 100 \quad \frac{RV - TV}{TV}$$

where RV = reported values
TV = true values

When RV = TV then %A = 0 indicating no deviation from the true answer.

TABLE I-1. PERFORMANCE AUDIT RESULTS: METHOD 5 METER BOXES

Meter box no.	% A	Average % A
11	-0.8	-0.9
11	-1.0	
11	-1.0	
9	1.1	1.3
9	1.0	
9	1.8	
7	0.2	0.3
7	0.3	
7	0.3	

The average percent accuracies were -0.9, 1.3, and 0.3% for meter boxes 7, 9, and 11.

The field performance audit summaries for the RAC sample boxes, NDIR, Orsat, etc., are given on Table I-2. The performance audit results are expressed as relative percent accuracy and were calculated from the above equation. Relative percent accuracy ranged from -6.1 to 2.5%. Eleven of the reported relative percent accuracies were between -3.0 and 3.0%.

TABLE I-2. FIELD PERFORMANCE AUDIT RESULTS SUMMARY

Parameter	Device audited	Device I.D.	Relative percent accuracy
Temperature	Sample box/Method 5	#5, position 1	+ 2.5
Temperature	Sample box/Method 5	#5, position 2	+ 2.5
Temperature	Sample box/Method 5	#5, position 3	- 0.2
Temperature	Sample box/Method 5	#11, position 2	0.0
Temperature	Sample box/Method 5	#11, position 3	- 2.1
Temperature	Sample box/Method 5	#11, position 1	- 2.1
Barometric pressure	Aneroid barometer	V-4029	- 0.0
CO	NDIR	7952	- 0.5
THC	Beckman 402	8736	- 6.1
O_2	Polarigraph	8206	+ 2.0
CO_2	Orsat	2865	- 4.2
O_2	Orsat	2865	- 2.1
Gas volume	Dry gas meter	9044	0.0

One problem was encountered. The audit device for the aneroid barometer check was defective. A check of the field barometer against a mercury barometer upon return from the field indicated that the field device was operating properly.

Field Systems Audit

Each major sampling station was audited once during the test period. All field work, however, could not be audited because of time constraints. A total of 326 individual items on nine system audits were examined. There were 29 negative findings recorded. Only one of these findings could have affected the quality of the data. The others were minor and did not affect data quality.

The one problem observed was associated with the determination of moisture on saturated stacks according to Method 4. Two methods are to be used for determining moisture. If the two values do not agree, the lower of the two values is used to calculate the isokinetic sampling rate. Based on the recorded stack temperature of 177°F, the maximum volume percent of water would be 47%. The value used was 52%.

One area of procedural weakness was in the chloride train operation. Of the 29 negative findings, 11 were associated with chloride train operation. The operator was not sufficiently familiar with the train and its operation to ensure maximum efficiency of operation. A more stringent training program should be instituted.

Another problem was the security of samples for chain of custody requirements. A number of negative recordings were associated with improper sample security.

LABORATORY AUDIT

Interlaboratory Performance Audit

The interlaboratory performance audit is intended to compare the results of the analysis of blind samples containing a number of compounds. The results of this audit are given in Table I-3. It is important to note that the samples were made up in acetone, which made analysis of certain compounds very difficult.

MRI correctly identified 11 of the 12 unknown compounds, and Rockwell identified 10 of 12. Based on an acceptance level of ± 25% of theoretical for accuracy, MRI was within limits on 17 of 24 possible, and Rockwell was within limits on 14 of 24 possible. The average relative precision and its standard deviation for MRI was 9.4 ± 7.4% and for Rockwell was 3.9 ± 1.5%. Thus, MRI was more accurate, but Rockwell was more precise.

The relative accuracy of MRI and Rockwell agreed 78.9% of the time at the ± 25% acceptance level. This means on any given analysis the chances are good that MRI and Rockwell will agree. Any disagreement is most probably caused by matrix effects or differences in the sample.

MRI Performance Audit

Chloride analysis results are presented in Table I-4. Two different methods were used to analyze these QA sample, namely, the Technicon Autoanalyzer and the titration method using bromophenol blue dicarbazone indicator. The results indicate the Autoanalyzer provided a more accurate and precise answer than did the volumetric method. Very little deviation was seen in any of the results for chlorides.

The objective of the MRI POHC audit was mainly to assess MRI analytical performance for organic chemicals and secondarily to examine the effectiveness of the polyethylene glycol method for volatile POHC analysis. The results of this audit are given on Table I-5. Only one determination, the result for carbon tetrachloride in Sample A, exceeded the ± 25% acceptance level for accuracy. The determination of carbon tetrachloride in Sample B was within the acceptance limits. The average precision and its standard deviation for two standard deviation units (2σ or the 95% probability level) was +0.73 to +23.12. No precision values were outside of this range.

Table I-6 summarizes the results of the analysis of three trace metals by hydride generation atomic absorption spectroscopy. Relative accuracies ranged from -12 to +27%. Relative precision ranged from 0 to +1.5%. There were three acceptable values and two unacceptable values based on EPA criteria (see footnote c, Table I-6). These criteria do not take into account matrix interference effects.

TABLE I-3. VOLATILE AND SEMIVOLATILE ANALYSIS RESULTS

Compound	Theoretical concentration (µg/ml)	QA solution[a]	Relative accuracy (%)[b]		Relative precision (%)[c]	
			MRI	Rockwell	MRI	Rockwell
Benzene	23	1	+135	+159	4	3
	109	2	-18	+22	23	3
Chloroform	108	1	+9	-14	3	3
	96	2	+15	-13	14	3
1,1-Dichloroethane	98	1	-19	-11	5	4
	22.5	2	+19	-1	9	3
trans-1,2-Dichloroethylene	17	1	+3	+7	3	7
	103	2	+7	-17	14	3
Hexachlorocyclopentadiene	106	1	-12	+46	5	8
	104	2	-19	+57	6	4
Hexachloroethane	91	1	-27	-27	5	4
	91	2	-25	-28	5	2
Isopropanol	107	1	f	f	f	f
	15	2	f	f	f	f
Methylene chloride	104	1	-30	-14	1	3
	96	2	-11	-12	25	4
Tetrachloroethylene	13	1	+1	+23[e]	4	e
	16	2	+8	d	7	d
1,1,1-Trichloroethane	17.5	1	-14	-8	6	5
	92	2	-5	-4	16	4
Trichloroethylene	18	1	-8	+1	5	5
	100	2	-29	-10	27	3
m-Xylene	15	1	+138	f	10	f
	16	2	+213	f	10	f

---

[a] QA solution No. 1 placed in vials numbered 3, 9, 11 and given to Rockwell. QA solution No. 2 placed in vials numbered 5, 8, 14 and given to Rockwell.

[b] Relative accuracy (%) = $\left[\dfrac{\dfrac{\Sigma C_R}{n} - C_T}{C_T}\right] \times 100$

where C_R = reported concentrations
n = number of reported concentrations
C_T = theoretical concentration

[c] Relative precision = average percent difference between reported duplicates.

[d] Results reported as not detected.

[e] One value given; others reported as not detectable.

[f] No results reported, compound not identified.

NOTE: MRI also reported the presence of carbon tetrachloride and hexachlorobutadiene. These compounds were not added to the QA samples prepared.

TABLE I-4. CHLORIDE ANALYSIS RESULTS

Parameter	Method audited	Theoretical concentration (meq)	QA solution	Relative accuracy (%)[a]	Relative precision (%)
Chloride	Autoanalyzer	0.094	1[b]	0	1.9
Chloride	Titration	0.094	1[b]	+12	3.95
Chloride	Autoanalyzer	0.204	2[c]	-1	1.9
Chloride	Titration	0.204	2[c]	+4	4.0

[a] Relative accuracy (%) = $\left[\frac{\frac{\Sigma C_R}{n} - C_T}{C_T}\right] \times 100$

where C_R = reported concentration

n = number of reported concentrations

C_T = theoretical concentration

[b] QA solution No. 1 placed in plastic containers labeled MSD Cl-1, MSD Cl-4.

[c] QA solution No. 2 placed in plastic containers labeled MSD Cl-2, MSD Cl-3.

TABLE I-5. RESULTS OF THE MRI PERFORMANCE AUDIT

Compound	QA Solution	Theoretical Concentration (μg/ml)	(%) Relative Accuracy[a]	(%) Relative Precision[b]
Chloroform	A	c	-	-
	B	634	7	18
1,1,1-Trichloroethane	A	269	19	4
	B	269	6	14
Carbon tetrachloride	A	758	28	4
	B	678	15	11
Tetrachloroethylene	A	664	-6	9
	B	664	-12	5
Pentachloroethane	A	305	4	4
	B	447	5	18
Hexachloroethane	A	594	4	16
	B	594	7	17
1,4 Dichlorobenzene	A	702	-6	17
	B	529	-11	16
Hexachlorocyclopentadiene	A	c	-	-
	B	512	15	14

[a] Relative accuracy (%) = $\dfrac{\dfrac{\Sigma C_R}{n} - C_T}{C_T} \times 100$

where C_R = reported concentration

n = number of reported concentrations

C_T = theoretical concentration

[b] Relative precision = average percent difference between reported values.

[c] Compound not added to this solution.

TABLE I-6. TRACE METAL ANALYSIS RESULTS

Parameter	Method audited	Theoretical concentration (mg/ml)	QA solution	Relative[a] accuracy (%)	Relative[b] precision (%)	EPA limits (%)	Acceptable data
As	AAS	41	APS-1	+27	0	-25 to +17	no
		74	APS-2	+16	0		yes
Hg	AAS	51	APS-1	-9	1.5%	-25 to +17	yes
		34	APS-2	-12	0		yes
Se	AAS	c	APS-1	-	-	-15 to +12	d
		39	APS-2	+18	1%		no

a Relative accuracy (%) = $\left[\dfrac{\dfrac{\Sigma C_R}{n} - C_T}{C_T}\right] \times 100$

where C_R = reported concentration

n = number of reported concentrations

C_T = theoretical concentration

b Relative precision = average percent difference between duplicates.

c Data obtained from EPA IFB WA81-H005, "Chemical Analytical Services for Metals and Inorganic Parameters, Appendix B, Quality Assurance Requirements."

d Element not added to QA solution.

MRI Systems Audit

The intent of the laboratory systems audit was to look at procedural aspects of the conduct of laboratory work. The phases of lab work examined were:

* Waste feed sample preparation for trace metals analysis

* ICP analysis of waste feed

* Extraction and computing of Modified Method 5 sample trains

* Volatile organics analysis by GC/MS

Generally speaking, the audit revealed that all laboratory practices were adequately performed. The systems audit looked at 150 individual items. There were eight negative findings, but they were all minor and did not affect the quality of the data. The most consistent negative finding was lack of adequate instructions for waste disposal. However, this is not an issue which impacts on data quality.

SECTION I-4

CONCLUSIONS

Overall, the performance and conduct of the field and laboratory work are judged to be adequate, and Test II is determined to be valid.

More specifically:

* The field performance audit determined the equipment was calibrated and that it performed adequately.

* The field systems audit determined that the protocols and procedures were adequately followed.

* The interlaboratory performance audit indicated acceptable correlation between the results from MRI and Rockwell.

* The chloride analysis was accurate and precise.

* The MRI POHC analysis was accurate and adequately precise.

* The trace metals analysis generally was marginally acceptable.

* Laboratory procedures were performed in an acceptable manner.

ATTACHMENT 1
FIELD SYSTEMS AUDIT FORM

Project No.: ____________________ Date: ____________________

Sampling Site: ____________________ Auditor: ____________________

Method: ____________________ Run No.: ____________________

Sample Type: ____________________ Form __________ of __________

- -

Presampling Preparation	Yes	No	NA	Comments
1. Written Protocol	___	___	___	____________________ ____________________
2. Sample Container Prep.	___	___	___	____________________ ____________________
3. Proper Equipment Cleaning	___	___	___	____________________ ____________________
4. Qualified Personnel	___	___	___	____________________ ____________________
5. Pretest Planning	___	___	___	____________________ ____________________
6. Equipment Maintainence	___	___	___	____________________ ____________________

SYSTEMS AUDIT FORM
PAGE 2

7. Equipment Calibrated ___ ___ ___ ______________________________

____

8. Calibration Documented ___ ___ ___ ______________________________

____

9. Team Fully Informed ___ ___ ___ ______________________________

____

10. Proper Sampling Location ___ ___ ___ ______________________________

____

11. Equipment Assembled ___ ___ ___ ______________________________

____

12. Equipment Checked ___ ___ ___ ______________________________

____

13. Spare Parts Available ___ ___ ___ ______________________________

____

14. Proper Forms Available ___ ___ ___ ______________________________

____

15. Proper Filter Media ___ ___ ___ ______________________________

____

16. Proper Preconditioning ___ ___ ___ ______________________________

____

17. Appropriate Records ___ ___ ___ ______________________________

____

18. Satisfactory Weighing ___ ___ ___ ______________________________

____

19. Proper Weighing Conditions ___ ___ ___ ______________________________

____

20. Proper Solution Preparation ___ ___ ___ ______________________________

____

21. Sampling Train Workmanship ___ ___ ___ ______________________________

____

22. Adequate QC ___ ___ ___ ______________________________

____

23. — — — ____________________

____

Sampling

24. Appropriate No. of People — — — ____________________

____

25. Proper Data Recording — — — ____________________

____

26. Proper Sampling Sequence — — — ____________________

____

27. Proper Procedure — — — ____________________

____

28. Leak Check Performed — — — ____________________

____

29. Adequate QC — — — ____________________

____

30. ___ ___ ___ ______________________________

____

Post Sampling

31. Proper Sample Recovery ___ ___ ___ ______________________________

____

32. Proper Labeling ___ ___ ___ ______________________________

____

33. Proper Storage ___ ___ ___ ______________________________

____

34. Adequate Blanks ___ ___ ___ ______________________________

____

35. Chain of Custody ___ ___ ___ ______________________________

____

36. Adequate QC ___ ___ ___ ______________________________

____

ATTACHMENT 2
LABORATORY SYSTEMS AUDIT FORM

Project No.: ____________________ Date: ____________________

Analysis Site: ____________________ Auditor: ____________________

Method: ____________________ Run No.: ____________________

Sample Type: ____________________ Form ________ of ________

Sample Preparation/Extraction	Yes	No	NA	Comments
Written protocol	___	___	___	____________________ ____________________
Qualified personnel	___	___	___	____________________ ____________________
Appropriate number of people	___	___	___	____________________ ____________________
Team fully informed	___	___	___	____________________ ____________________
Appropriate records	___	___	___	____________________ ____________________
Satisfactory weighing	___	___	___	____________________ ____________________
Proper weighing conditiongs	___	___	___	____________________ ____________________
Proper solution preparation	___	___	___	____________________ ____________________
Proper sample preparation	___	___	___	____________________ ____________________ ____________________

SYSTEMS AUDIT FORM
PAGE 2

Proper data recording ___ ___ ___ ____________________
____

Proper labeling ___ ___ ___ ____________________
____

Proper storage ___ ___ ___ ____________________
____

Adequate blanks ___ ___ ___ ____________________
____

Proper disposal methods ___ ___ ___ ____________________
____

Proper forms available ___ ___ ___ ____________________
____

Proper reagent purity ___ ___ ___ ____________________
____

Proper standards preparation ___ ___ ___ ____________________
____

Proper spiking procedure ___ ___ ___ ____________________
____

Sample Analysis/Quantitation

Planning ___ ___ ___ ____________________
____

Written protocol ___ ___ ___ ____________________
____

SYSTEMS AUDIT FORM
PAGE 3

Qualified personnel ___ ___ ___ ____________________
____

Appropriate number of people ___ ___ ___ ____________________
____

Team fully informed ___ ___ ___ ____________________
____

Proper equipment maintenance ___ ___ ___ ____________________
____

Proper equipment cleaning ___ ___ ___ ____________________
____

Equipment calibrated ___ ___ ___ ____________________
____

Calibration documented ___ ___ ___ ____________________
____

Spare parts available ___ ___ ___ ____________________
____

Analysis procedure documented ___ ___ ___ ____________________
____

Proper forms available ___ ___ ___ ____________________
____

Proper data recording ___ ___ ___ ____________________
____

Quantitation sequence documented ___ ___ ___ ____________________
____

Adequate blanks ___ ___ ___ ____________________

____

Adequate QC samples ___ ___ ___ ____________________

____

Proper disposal methods ___ ___ ___ ____________________

____

APPENDIX J

QUALITY ASSURANCE PROCEDURES AND RESULTS

Strict quality assurance (QA) procedures were followed for the analysis aspects of this program. The objective of the QA activities was to provide data of known quality by making certain that the chemical analyses were performed under controlled conditions and also to ensure that the experimental work was recorded for archival storage.

The data generated by the analytical laboratory are extremely important because they are used for decision-making regarding the incineration of hazardous waste. The degree of confidence that can be placed in the data was determined from precision and accuracy (recovery) data generated during the program.

Precision refers to the reproducibility of replicate measurements, from both the anaysis of the calibration standards used to quantify the samples and from the replicate analysis of actual samples and fortified samples.

Accuracy refers to the difference between an analytical result and the known value for a sample. This type of data was generated by fortifying measured amounts of POHCs into some of the samples, followed by extraction and analysis to determine the recovery of the fortified compounds.

The aspects of the QA procedures, including sample tracking, documentation procedures, tuning and calibration of the instruments, blank preparation and analysis, spiking and fortification procedures, and general precision and accuracy of the analyses are discussed in the sections below.

SAMPLE TRACKING AND PREPARATION

The sample tracking and preparation information is primarily recorded in the laboratory record book (LRB). Examples of the type of information recorded in the LRB are the dates the samples were received and prepared, the location, condition, and temperature of storage of the samples, and summaries of the analytical procedures used.

Each sample extract label retains the original sample designation (i.e., WF(6)-2) along with designations of the solvent, a designation of whether the extract is to be analyzed for volatiles or semivolatiles, MRI project number, dates, and the initials of the chemist who prepared the samples.

The samples submitted for GC/MS analysis were stored in a refrigerator in the GC/MS laboratory. The backlog of samples kept in the GC/MS lab was kept to a minimum, i.e., only 1 to 2 days of analysis time. The samples were then returned to the principal storage area in the hazardous waste/sludge lab following GC/MS analysis.

DOCUMENTATION PROCEDURES

The documents for this program include the final report, letters of transmittal, records of telephone conversations relative to the program, and all data and records associated with work on this program.

A tremendous quantity of data and information was generated during this program in addition to the above, including the following:

Date of GC/MS analyses
All volumes and weights used
Dilution and concentration factors
Amounts of internal standards used
Internal standard area response
Injection volumes
Relative response factors used for quantification
Scan number and retention time of GC/MS peaks
Most intense mass spectral fragmentations
Absolute and/or relative retention time
Compound identifications
Total ion chromatograms
Library search results
9-Track tape storage files of all GC/MS data
Results of analysis of calibration standards
Mass spectrometer tuning results
Instrument maintenance records

Most of the data and information is contained in the computer hard-copied output, in the LRB's, and on chromatograms.

Some additional details of the documentation procedures include the following:

* One project LRB was used to record all information pertaining to sample extraction, and preparation for GC/MS analysis.

* The details of the GC/MS analyses were recorded in notebooks assigned to each GC/MS instrument.

* GC/MS data were taped at regular intervals (i.e., weekly) to provide a backup to the data on disk and for permanent storage of the data at the end of the program.

- All GC/MS computer output was placed into file folders labeled with sample number and project number and stored with the analytical task leader at the end of the project.

- The project LRB will be archived in a vault at the end of the program.

- The GC/MS notebooks are stored by the GC/MS facility manager.

INSTRUMENTATION

Specific tuning and calibration procedures were followed for the analytical instrumentation as described below.

Mass Spectrometer Tuning and Calibration rPocedures

Three mass spectrometers were used to analyze samples for POHCs. A Finnigan 4000 and a Varian CH4 were used to measure volatile POHCs. The Finnigan 4000 and a Varian MAT 311A were used to measure semivolatile POHCs. The Finnigan 4000 is a quadrupole instrument and the Varian CH4 and the Varian MAT 311A are magnetic sector instruments. The Finnigan 4000 was tuned (set high/low mass spectral balance) using perfluorotributylamine (FC-43). The tuning and sensitivity was checked prior to each day's sample data acquisition by analyzing a calibration standard containing about 20 ng of decafluorotriphenylphosphine (DFTPP). The DFTPP ion balance criteria which were met, except for intermittent excess sensitivity at m/e 51, are listed in EPA Method 625 and in the A. D. Little manual. It is sometimes difficult to keep m/e 51 below 60% due to a background interference in the mass spectrometer.

The two magnetic sector instruments were calibrated using perfluorokerosine (PFK). The tuning of the magnetic sector instruments cannot be adjusted as with the quadrupole instrument. The ion balance for p-bromofluorobenzene (BFB), the tuning criteria compound for analysis of volatile organic compounds in EPA Method 624, was met for analysis of the volatile POHCs on the Varian CH4. However, the Varian 311A gave a DFTPP ion abundance with excess sensitivity at high mass range. This is common with magnetic sector instruments and presented no problem in identifying and quantifying sample components because the tuning remained constant for all calibration standard and sample analyses.

The FC-43 and PFK described above were used to calibrate the masses of the mass spectrometers. However, the response of the GC/MS instruments for the analysis of the POHCs was calibrated by analyzing standard solutions (solutions of known concentration) prepared by weighing known amounts of the pure authentic compounds. Several concentrations of the standard solutions were analyzed. At least one standard solution was analyzed each day that samples were analyzed.

ICP and AAS Calibration

All 30 detection channels for the Jarrell-Ash Mark III ICP emission spectrometer were calibrated with mixed standards containing 28 elements. Iron and aluminum have two channels.

A blank and 10-ppm standard were used to calibrate each channel. A 100-ppm standard was used to calibrate the less sensitive Na channel.

The following steps summarize the calibration procedure performed each day:

1. Turn on instrument and initiate a stable ICP argon plasma.

2. After 30 min, aspirate a 1-ppm Cd solution and adjust the spectrometer entrance slit for maximum emission intensity. Now, the optical alignment is optimum for the best signal/noise for all channels.

3. Record the date, time, name, slit micrometer setting, low voltage current, and room temperature in the Mark III Instrument Log Book.

4. Aspirate each of the five calibration mixed standards, perform three 10-sec integrations, and use mean results to calibrate the channels.

5. Repeat step 3. Confirm the accuracy of the initial calibration by printing out the mean results in concentration mode.

6. If the concentration for the calibration standard during step 5 is more than ± 2% of the true value, recalibrate the instrument.

7. Confirm the accuracy of the calibration by analyzing a multielement instrument check sample. All channels should give values within ± 5% of the true values. Otherwise, recalibrate the instrument.

8. Analyze the instrument check sample at least every 20th determination. If the measured values are not within ± 5% of the true values, recalibrate the instrument and repeat all analyses since the last check sample that was in control.

For analysis of arsenic by atomic absorption spectroscopy (AAS), a Fisher Scientific commercial arsenic stock solution (1,000 μg/ml) was used to prepare aqueous calibration standards. The standards were prepared in a 30% (v/v) HCl matrix to approximate the sample matrix as closely as possible. At the time of analysis, 5% (w/v) potassium iodide was added to all samples and standards to optimize the arsenic response.

The calibration curves generated by this method were linear to 200-ng arsenic, with a relative standard deviation of the standards ranging from 6 to 8% RSD.

For analysis of selenium by AAS, a Fisher Scientific commercial selenium stock solution (1,000 µg/ml) was used to prepare aqueous calibration standards. The standards were prepared in a 25% (v/v) HCl matrix to approximate the sample matrix as closely as possible.

The calibration curves generated by this method were linear up to 300 ng selenium, with a relative standard deviation of the standards ranging from 8 to 11% RSD.

For analysis of mercury by AAS, a Fisher Scientific commercial mercury stock solution (1,000 µg/ml) was used to prepare aqueous calibration standards. The standards were prepared in a 10% (v/v) HNO_3 matrix to approximate the sample matrix as closely as possible.

The calibration curves generated by this method were linear to 1,000 ng mercury, with relative standard deviation values of the standards ranging from 3 to 7% RSD.

PRECISION AND RECOVERY STUDIES

POHCs

Mass Spectrometric Response Factors--

A measure of the expected variability around a single measurement of an analyte in a sample can be determined from the precision of replicate analyses of the calibration standards.

Tables J-1 and J-2 list the average relative mass spectrometric response factors for the two sets of volatile POHCs selected for the two different trial burns (Tests 1-6 and Tests 7-9). Also included in the table are the frequency of analyses and the percent relative standard deviations of the responses.

A desirable limit on the percent relative standard deviations for a large number of analyses is in the range of 20 to 25%. Most of the values were in this range, except that the carbon tetrachloride values were more variable than desired for the first set of POHCs (Table J-1) and the secondary ions for chloroform and 1,1,2,2-tetrachloroethane were more variable than desired for the second set of POHCs (Table J-2).

Tables J-3 and J-4 list the average response factors, frequency of analyses, and the percent relative standard deviation of the response factors for the most frequently analyzed calibration standards containing the semivolatile POHCs and surrogate compounds for the two sets of tests. The frequency of analysis, average response factor, and percent relative standard deviation for all the calibration standards are also given. Again most of the percent relative standard deviations were within the desired 25% range for the analysis of this large number of calibration standards.

TABLE J-1. RELATIVE RESPONSE FACTORS FOR VOLATILE POHCs ANALYZED ON FINNIGAN 4000, OCTOBER 29 TO NOVEMBER 2, 1981

		100-ng standard			Average of all concentrations[a]		
Analyte	Ion m/e	No. of entries	Average RRF[b]	% Relative standard deviation	No. of entries	Average RRF[b]	% Relative standard deviation
Chloroform	83	6	1.10	12	9	1.07	15
Carbon tetrachloride	117	6	0.450	21	9	0.411	28
Tetrachloroethylene	166	6	0.640	4	9	0.662	15

[a] 50-, 100-, 200-, and 250-ng standards.

[b] Mass spectrometric response factor of given compound relative to the internal standard, 2-bromo-1-chloropropane.

TABLE J-2. RELATIVE RESPONSE FACTORS FOR VOLATILE POHCs ANALYZED ON VARIAN CH4, OCTOBER 30 TO DECEMBER 12, 1981

		100-μg/μl standard			Average of all concentrations[a]		
Analyte	Ion m/e	No. of entries	Average RRF[b]	% Relative standard deviation	No. of entries	Average RRF[b]	% Relative standard deviation
Chloroform	83	15	1.02	11	27	1.01	19
	118	8	0.008[c]	33	11	0.007	43
	85	6	0.617[c]	16	11	0.582	24
Carbon tetrachloride	117	16	0.442	15	28	0.450	15
Tetrachloroethylene	166	12	0.888	13	19	0.899	11
	164	8	0.685[c]	6	15	0.695	9
1,1,1-Trichloroethane	97	10	0.527	17	20	0.563	19
1,1,2-Trichloroethane	97	7	0.630	5	13	0.628	5
1,1,2,2-Tetrachloroethane	83	5	1.20	8	6	1.18	8
	95	4	0.198[c]	46	10	0.221	44
1,1,1,2-Tetrachloroethane	131	6	0.435	13	9	0.428	14

[a] 50-, 100-, 200-, and 250-ng standards.

[b] Mass spectrometric response factor relative to 2-bromo-1-chloropropane internal standard.

[c] These secondary ions were used for quantification of sample components when the primary ions saturated.

TABLE J-3. RELATIVE RESPONSE FACTORS FOR SEMIVOLATILE POHCs ANALYZED ON FINNIGAN 4000, NOVEMBER 11 THROUGH 25, 1981

	20-ng/μl standard			100-ng/μl standard			Average of all concentrations[a]		
Compound	No. of entries	Average RRF[b]	Percent relative standard deviation	No. of entries	Average RRF[b]	Percent relative standard deviation	No. of entries	Average RRF[b]	Percent relative standard deviation
Pentachloroethane	10	0.249	22	13	0.249	18	23	0.249	21
Hexachloroethane	10	0.236	19	13	0.232	17	23	0.233	18
1,2-Dichlorobenzene	10	0.740	18	13	0.755	19	23	0.749	18
1,3-Dichlorobenzene	10	0.709	23	13	0.749	20	23	0.732	21
1,4-Dichlorobenzene	10	0.712	18	13	0.813	19	23	0.769	20
Hexachlorocyclopentadiene	10	0.166	37	13	0.205	26	23	0.188	31
Hexachlorobenzene	10	0.285	14	13	0.276	18	23	0.280	16
Decafluorobiphenyl	10	0.31	19	10	0.253	31	20	0.282	26
d_8-Naphthalene	10	4.24	13	13	3.02	20	23	3.516	23
d_{12}-Chrysene	10	0.526	37	13	0.918	12	23	0.748	33

---

[a] 10-, 20-, 100-, and 200-ng standards.

[b] Mass spectrometric response factors relative to D_{10}-anthracene internal standard.

TABLE J-4. RELATIVE RESPONSE FACTORS FOR SEMIVOLATILE POHCs ANALYZED ON VARIAN 311A, NOVEMBER 9 THROUGH 17, 1981

Compound	10-ng/µl standard			Average of all concentrations[a]		
	No. of entries	Average RRF[b]	Percent relative standard deviation	No. of entries	Average RRF[b]	Percent relative standard deviation
Pentachloroethane	8	0.163	25	14	0.151	26
Hexachloroethane	7	0.189	13	13	0.172	20
1,2-Dichlorobenzene	7	0.494	9	10	0.459	17
1,3-Dichlorobenzene	6	0.853	45	10	0.71	51
1,4-Dichlorobenzene	6	0.505	19	9	0.456	25
Hexachlorocyclopentadiene	8	0.186	32	14	0.198	30
Hexachlorobenzene	8	0.526	5	14	0.491	10
Decafluorobiphenyl	7	1.04	15	12	0.935	20
d_8-Naphthalene	7	2.66	7	13	2.023	39
d_{12}-Chrysene	8	1.96	32	13	1.72	34

[a] 10-, 20-, 100-, and 200-ng standards.

[b] Mass spectrometric response factors relative to D_{10}-anthracene internal standard.

Analysis of Replicates--

Several of the different types of samples generated on this program were analyzed in replicate to determine reproducibility. Gas samples and aqueous samples are, of course, homogeneous and problems with replication would have to be due to the sample preparation and analysis steps. The waste feeds samples, however, are not homogeneous and must be mixed prior to analysis.

Replicate analysis data for the waste feed samples were obtained by MRI from the replicate analyses of some of the fortified waste feed samples, as is discussed later. Waste feed sample WF(6)-2 was analyzed in duplicate, WF(6)-3 in triplicate, and WF(6)-8 in duplicate, based on fortifications of separate aliquots. These results for the selected POHCs are discussed later. However, analyses of these replicates also included non-POHCs. Table J-5 lists the quantitative precision of several of the non-POHC compounds, both volatile and semivolatile, found in the waste feed samples. (Non-POHC compounds refer to compounds which may be on the POHC list, but were not selected as POHCs for this program.) The quantification was accomplished by dividing the area counts from the enhanced (background subtracted) mass spectrum of the compound of interest by the area counts from the enhanced mass spectrum of the internal standard spiked into the sample extract, and then multiplying the result by the concentration represented by the internal standard relative to the original sample. The quantitative values were not corrected by applying exact mass spectrometric response factors because authentic calibration standards were not analyzed for these compounds. However, the primary interest was in the precision of the analyses and any adjustments in the quantification would not be significant.

The percent relative deviations shown in Table J-5 are, in general, quite similar, and in the 10 to 30% range. This suggests that the differences in the analysis results are primarily due to the variability in the analysis step although there could be slight variability in the samples, especially for waste feed sample WF(6)-2 where the percent RSDs for three of the compounds are near 50%, significantly higher than the RSDs for the other samples or for the response factors. The RSDs for the other compounds in this sample are not as high, however. Thus, it is possible that sample WF(6)-2 did not mix as well as WF(6)-5 and WF(6)-8 prior to aliquoting and analysis.

Table J-6 lists the results of analysis of duplicate gas bag samples, bottom ash samples, and scrubber effluent samples. The reproducibility of the analyses for these homogeneous samples was very good.

Recovery of POHC Fortifications--

Several fortification experiments were performed in which the POHCs were spiked into waste feed samples, into aqueous samples, and onto filter and XAD-2 resin samples. The waste feed samples were fortified with the undiluted POHCs by placing a weighed amount (several grams) of waste (enough for replicate analyses for volatiles and semivolatiles) and weighed amounts of the POHCs into vials each containing two stainless steel balls. The vials were then rotated overnight at 4°C on a roller mill. Aqueous samples

TABLE J-5. ANALYSIS PRECISION ON NON-POHC COMPOUNDS IN REPLICATE WASTE FEED SAMPLES

Compound	Concentration, µg/g												
	WF(6)-2				WF(6)-5					WF(6)-8			
	Replicate 1	Replicate 2	$\bar{x}$	% RSD	Replicate 1	Replicate 2	Replicate 3	$\bar{x}$	% RSD	Replicate 1	Replicate 2	$\bar{x}$	% RSD
Diethyl ether	1,000	690	870	29	880	920	(a)	900	3.1	290	300	300	2.4
Trichloroethylene	500	370	440	21	1,400	1,400	1,800	1,500	16	22,000	16,000	19,000	22
Benzene	2,500	1,200	1,900	49	1,800	1,300	2,900	2,000	41	8,200	5,300	6,800	30
Toluene	18,000	13,000	15,000	25	11,000	11,000	18,000	13,000	33	30,000	21,000	26,000	24
Chlorobenzene	6,210	5,000	5,600	15	2,400	2,700	4,400	3,200	35	28,000	23,000	26,000	14
Isophorone	550	260	410	51	290	300	400	330	18	400	290	350	23
Naphthalene	560	270	420	50	680	700	850	740	13	300	260	280	10
Chlorotoluene	520	380	450	22	380	400	470	420	11	150	120	140	16
Isodrin	620	450	540	23	440	300	490	410	24	240	160	200	28

[a] This sample gave an aberrantly high value due to a coeluting peak.

TABLE J-6. RESULTS OF ANALYSIS OF DUPLICATE SAMPLES FOR VOLATILE POHCs AND PICs

Analyte	IGS-7 (μg/m^3)	IGS-9 (μg/m^3)	BA-4 (μg/ℓ)	SE-6 (μg/ℓ)
Chloroform			4/6	< 1/< 1
Carbon tetrachloride			< 1/< 1	< 1/< 1
Tetrachloroethylene			2/2	< 1/< 1
1,1,1-Trichloroethane	30/30	< 1/< 1		
1,1,2-Trichloroethane	< 1/< 1	< 1/< 1		
1,1,1,2-Tetrachloroethane	< 1/< 1	< 1/< 1		
1,1,2,2-Tetrachloroethane	< 1/< 1	< 1/< 1		
Bromodichloromethane	45/48	9/13		
Bromoform	12/13	2/3		
Dibromochloromethane	18/17	9/10		

were spiked with methanolic solutions of the POHCs and stored at 4°C overnight prior to extraction. XAD-2 resin samples were spiked with the methanolic solution and allowed to dry for several hours.

Table J-7 lists the results of analysis from fortifying several waste feed samples with volatile POHCs. Duplicate aliquots of waste feed samples WF(6)-2 and WF(6)-8 were fortified with the volatile POHCs at approximately five times the unfortified concentration. Triplicate aliquots of waste feed sample WF(6)-5 were also fortified with volatile POHCs. These are the same samples for which the precision of the unspiked compounds was given in Table J-5. The percent recoveries listed in Table J-7 were calculated using the following formula:

$$\text{Percent Recovery} = \frac{\text{Concentration in fortified sample} - \text{concentration in unfortified sample}}{\text{fortification level}}$$

The good recovery values suggest that the concentrations determined for the volatile POHC analytes in the unfortified waste feed samples were quite accurate. The precision of the replicate analyses was also quite good.

The results of the duplicate analyses when volatile POHCs were fortified into aqueous bottom ash and scrubber effluent samples are shown in Table J-8. Carbon tetrachloride yielded fairly low recoveries, possibly associated with a matrix effect with the samples, but the rest of the results were good.

The percent recovery of semivolatile POHCs spiked into waste feed samples is given in Table J-9. Two of the waste feed samples were spiked in duplicate and one in triplicate at the levels indicated. Generally the recoveries were too high based on the analysis of the unfortified sample and also not as precise as for the fortification experiments with the volatile POHCs. The results suggest that the analyses of the unfortified samples may have given somewhat low results, possibly due to a matrix effect with the sample.

Table J-10 lists the results of the analyses when semivolatile POHCs were spiked into aqueous Modified Method 5 train samples and onto clean XAD-2 resin. The recoveries were quite precise, but somewhat lower than expected. Data in Table J-10 were based on a benzene-methanol mixture as the solvent for extraction in XAD resin. As indicated earlier, EPA authority indicated that methylene chloride should have been used. A subsequent experiment for recovery comparison between benzene-methanol and methylene chloride indicated that methylene chloride gave better recoveres for most POHCs.

TABLE J-7. RECOVERIES OF VOLATILE POHCs IN FORTIFIED WASTE FEED SAMPLES

Analyte	Waste feed WF(6)-2			Waste feed WF(6)-5				Waste feed WF(6)-8		
	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]	Fortification replicate 3 (% recovery)[a]	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]
Chloroform	9,900	130	97	50,000	90	95	93	a	-	-
Carbon tetrachloride	10,000	100	81	19,000	78	89	78	a	-	-
1,1,1-Trichloroethane	b	-	-	b	-	-	-	73,000	130	c
1,1,2-Trichloroethane	b	-	-	b	-	-	-	15,000	110	110
1,1,1,2-Tetrachloroethane	b	-	-	b	-	-	-	10,000	100	95
1,1,2,2-Tetrachloroethane	b	-	-	b	-	-	-	10,000	110	110
Tetrachloroethylene	9,900	97	77	9,800	82	86	85	b	-	-

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[a] Percent recovery = $\frac{\text{Concentration in fortified sample - Concentration in unfortified sample}}{\text{Spiking level}} \times 100$

[b] This compound was not a POHC to be fortified in these samples.

[c] This sample was inadvertently not fortified with this compound.

TABLE J-8. RECOVERY OF VOLATILE POHCs IN FORTIFIED BOTTOM ASH AND SCRUBBER EFFLUENT SAMPLES

Analyte	Spiking level (μg/ℓ)	Bottom ash BA-2 (% recovery)[a]	Scrubber effluent SE-2 (% recovery)[a]
Chloroform	2	97, 120[b]	120, 140[b]
Carbon tetrachloride	2	47, 67[b]	60, 85[b]
Tetrachloroethylene	2	110, 110[b]	100, 70[b]

[a] $\% \text{ recovery} = \frac{\text{Conc. in fortified sample - Conc. in unfortified sample}}{\text{Spiking level}} \times 100$

[b] Results of duplicate analyses.

TABLE J-9. RECOVERY OF SEMIVOLATILE POHCs IN FORTIFIED WASTE FEED SAMPLES

	Waste feed WF(6)-2			Waste feed WF(6)-5				Waste feed WF(6)-8		
Analyte	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]	Fortification replicate 3 (% recovery)[a]	Spiking level (μg/g)	Fortification replicate 1 (% recovery)[a]	Fortification replicate 2 (% recovery)[a]
Pentachloroethane	b	-	-	b	-	-	-	1,000	211	178
1,2-Dichlorobenzene	b	-	-	b	-	-	-	1,500	226	192
Hexachloroethane	1,000	121	183	1,000	109	102	98	b	-	-
Hexachlorocyclopentadiene	25,000	113	117	24,000	109	134	120	b	-	-
Hexachlorobenzene	500	c	112	1,000	146	148	c	5,500	150	120

[a] $\text{Percent recovery} = \frac{\text{Concentration in fortified sample - Concentration in unfortified sample}}{\text{Spiking level}} \times 100$

[b] This compound was not a POHC to be fortified in this sample.

[c] The percent recoveries were 3 to 6 times higher than the duplicate sample. The unexpectedly high value may have resulted from a weighing error, but otherwise cannot be explained.

TABLE J-10. RECOVERY OF SEMIVOLATILE POHCs IN FORTIFIED METHOD 5 TRAIN SAMPLES

Compound	Spiking level total μg	Condensate spike No. 1 M5(6)-2B-Cond.[a] % recovery[b]	Condensate spike No. 2 M5(6)-3B-Cond.[a] % recovery[b]	Condensate spike No. 3 M5(6)-4A-Cond.[a] % recovery[b]	Condensate spike No. 4 M5(6)-9A-Cond.[a] % recovery[b]	Resin spike No. 1 % recovery[b]	Resin spike No. 2 % recovery[b]	Resin spike No. 3 % recovery[b]	Resin spike No. 4 % recovery[b]
Pentachloroethane	60	27	21	20	18	37	37	40	44
1,3-Dichlorobenzene	54	36	20	19	17	39	40	34	38
1,4-Dichlorobenzene	52	35	22	22	21	30	36	36	56
1,2-Dichlorobenzene	55	34	25	23	21	36	38	30	51
Hexachloroethane	50	29	29	26	18	38	39	44	45
Hexachlorocyclopentadiene	50	37	20	19	25	56	56	45	68
Hexachlorobenzene	42	43	43	39	25	51	47	53	55

[a] One-liter portions of condensate were fortified.

[b] Percent recovery = $\frac{\text{Concentration in fortified sample - Concentration in unfortified sample}}{\text{Spike level}} \times 100$

Spiking experiments, especially for solid matrices, may not provide the desired information, i.e., analyte extraction efficiency. For example, it was determined that when particulate collection filters were fortified with POHCs in a small volume of spikng solution, almost none of the POHCs, except for hexachlorobenzene, could be recovered, apparently due to rapid volatilization of the liquid compounds from a substrate for which they have little or no affinity. Vaporization losses or irreversible adsorption onto the dry XAD-2 resin may cause the low recoveries of the semivolatile POHCs from the XAD-2 resin. Fortification of aqueous samples is definitely valid, but also gave relatively low results, either due to a matrix effect causing low extraction efficiencies from the actual condensate samples or due to volatilization losses during Kuderna-Danish concentration of the methylene chloride extracts.

Table J-11 lists the analysis results from POHC fortifications of bottom ash and scrubber effluent samples. As with the condensate samples, the recoveries were quite low, either due to a matrix effect precluding high solvent extraction efficiency, evaporative losses during Kuderna-Danish concentration, adsorptive losses to the walls of the sample container, or headspace losses, although the headspace losses or evaporative losses seem unlikely for hexachlorobenzene.

Recovery of Surrogate Fortifications--

The aqueous, filter, and XAD-2 resin samples were spiked with surrogate compounds in order to attempt to monitor the extraction efficiencies. However, as described above, the spiking technique that was used for solid matrices allowed most of the surrogate compounds, as well as the POHC fortification compounds, to evaporate prior to extraction. The only successful surrogate spiking was achieved for aqueous samples where decafluorobiphenyl was the surrogate used at a spike concentration of 100 μg/liter. The percent recoveries of the decafluorobiphenyl from all of the aqueous samples are given in Table J-12. The recoveries are fairly low and similar to the recoveries experienced with the POHC fortifications into aqueous samples.

Method Blanks--

Method blank samples were generated for each type of sample matrix analyzed. Four method blanks were prepared and analyzed using the aqueous sample extraction techniques and four method blanks were prepared and analyzed using the filter and resin Soxhlet extraction techniques. However, there were no method blanks associated with the waste feed and Method 5 probe rinse samples.

Blind Samples--

The analysis of blind samples was an integral part of the QA activities associated with this program. Samples were received from the MRI QA manager and also from the EPA project officer. The results of the MRI sample analyses are discussed in Appendix I. The blind QA data for the EPA samples were all in the acceptable range. The precision and accuracy of the analyses of blind samples were in general very good and suggest that the data for this program were acquired under controlled conditions and interpreted correctly.

TABLE J-11. RECOVERY OF SEMIVOLATILE POHCs IN FORTIFIED BOTTOM ASH AND SCRUBBER EFFLUENT SAMPLES

Analyte	Spiking level (μg/ℓ)	Bottom ash BA-8 (% recovery)[a,b]	Scrubber effluent SE-7 (% recovery)[a,b]
Pentachloroethane	119	20	7
1,3-Dichlorobenzene	108	22	32
1,4-Dichlorobenzene	104	23	35
1,2-Dichlorobenzene	110	22	37
Hexachloroethane	99	30	33
Hexachlorocyclopentadiene	100	17	35
Hexachlorobenzene	84	30	45

[a] $$\% \text{ recovery} = \frac{\text{Conc. in fortified sample - Conc. in unfortified sample}}{\text{Spiking level}} \times 100$$

[b] Results of single determination.

TABLE J-12. RECOVERY OF SEMIVOLATILE SURROGATE COMPOUNDS IN AQUEOUS SAMPLES

Sample No.	% Recovery, decafluorobiphenyl
M5(6)-1A	a
M5(6)-1B	a
M5(2)-1A	43
M5(2)-1B	91
M5(6)-2A	a
M5(6)-2B	a
M5(2)-2A	6
M5(2)-2B	27
M5(6)-3A	a
M5(6)-3B	a
M5(2)-3A	73
M5(2)-3B	88
M5(6)-4A	43
M5(6)-4B	0
M5(2)-4A	0
M5(2)-4B	148
M5(6)-5A	0
M5(6)-5B-Condensate	47
M5(2)-5A	6
M5(2)-5B	0
M5(6)-6A	0, 0[b]
M5(6)-6B	0
M5(2)-6A	5
M5(2)-6B	0
M5(6)-7A	c
M5(6)-7B	c
M5(2)-7A	6
M5(2)-7B	0
M5(6)-8A	c
M5(6)-8B-Condensate	c
M5(2)-8A	57
M5(2)-8B	127
M5(6)-9A	c
M5(6)-9B	c
M5(2)-9A	1
M5(2)-9B	144

(Continued)

TABLE J-12. (continued)

Sample No.	% Recovery, decafluorobiphenyl
M5(6)-2B-Cond. Spike	61
M5(6)-9A-Cond. Spike	40
M5(6)-3B-Cond. Spike	36
M5(6)-4A-Cond. Spike	32
SE-1	32
SE-2	17
SE-3	47
SE-4	36
SE-5	23
SE-6	33
SE-8	13
SE-8	14
SE-9	9
BA-1	31
BA-2	26
BA-3	29
BA-4	19
BA-5	42
BA-6	27
BA-7	21
BA-8	33
BA-9	10
MW-2	36
MW-8	34
SE-Spike	68
BA-Spike	27

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[a] Decafluorobiphenyl was fortified in the Method 5 filter and resin samples as well as condensates. Consequently, representative percent recoveries could not be calculated.

[b] Results of duplicate analysis of extract.

[c] Decafluorobiphenyl was not fortified in this sample.

Detection Limits--

Based on the sample sizes, final extract volumes, extraction efficiencies, and detectable amounts of a given compound injected onto a GC column, the estimated detection limits for the GC/MS analyses of POHCs and PICs are given in Table J-13.

Metals

Duplicate Analyses--

For the metals analyses, 10% duplicate samples were prepared using 1-g aliquots at the time of sample digestion.

The results of duplicate metals analyses are listed in Table J-14. The liquid portion of waste feed samples WF(G)-1, WF(G)-3, WF(2)-6B, and WF(2)-7B were prepared and analyzed in duplicate. The solid portions of waste feed samples WF(6)-1 and WF(6)-9 were prepared and analyzed in duplicate. Five persulfate samples from the Method 5 sampling trains including MS(2)-2B, MS(2)-4A, MS(6)-6B, MS(6)-7B, and MS(6)-9B were also prepared and analyzed in duplicate.

The precision of the analysis is generally quite good although there are examples, just as with the POHC analysis, where the difference in the values vary by a factor of two or three and may result from matrix effects or interferences within the samples.

Recovery of Metal Fortifications--

Tables J-15 and J-16 list the recoveries of metals in waste feed samples and Method 5 train persulfate impinger samples. The waste feed samples listed in Table J-15 are divided between liquid and solid fractions of the waste. The liquid portions of four waste feed samples WF(6)-1, WF(G)-3, WF(2)-6B and WF(G)-9 were fortified with all 12 metals at about twice the unfortified concentration. Recoveries are reported in Table J-15 for all metals except silver, which was not recovered from any of the fortified waste feed samples. The low silver recovery may have been due to excess chloride in the waste which precipitated the silver as an insoluble salt. The solid portions of waste feeds WF(6)-3 and WF(6)-8 were also fortified with all 12 metals. The fortification level for the solid portions was determined by the level of metals determined in the liquid portions. As noted in Table J-15, this fortification level was too low for several metals.

Five Method 5 train persulfate impinger samples were fortified with the three volatile metals. The recoveries from these fortified samples are presented in Table J-16. The arsenic and mercury recoveries were quite consistent. A significant difference in selenium recoveries can be seen, however, between the fortified samples from tests 1, 3 and 5, and those from tests 8 and 9. The persulfate impingers from tests 7 through 9 contained no silver, so the pH of the digestate could be adjusted to give optimum selenium recoveries, thus causing the noticably higher recoveries from M5(2)-8A and M5(2)-9A.

TABLE J-13. ESTIMATED DETECTION LIMITS FOR POHCs AND PICs

Analyte	Sample type				
	Waste feed (µg/g)	Fuel oil (µg/g)	Integrated gas samples (µg/m^3)	Method 5 train samples (µg)	Scrubber effluent/ bottom ash (µg/ℓ)
Chloroform	10	10	1	b	1
Carbon tetrachloride	10	10	1	b	1
Tetrachloroethylene	10	10	1	b	1
1,1,1-Trichloroethane	10	10	1	b	1
1,1,2-Trichloroethane	10	10	1	b	1
1,1,2,2-Tetrachloroethane	10	10	1	b	1
1,1,1,2-Tetrachloroethane	10	10	1	b	1
Bromodichloromethane	10	10	1	b	1
Pentachloroethane	100	100	a	1	2.5
Hexachloromethane	100	100	a	1	2.5
1,2-Dichlorobenzene	100	100	a	1	2.5
1.3-Dichlorobenzene	100	100	a	1	2.5
1,4-Dichlorobenzene	100	100	a	1	2.5
Hexachlorobenzene	100	100	a	1	2.5
Hexachlorocyclopentadiene	500	500	a	5	5
Bromoform	10	10	1	b	5
Dibromochloromethane	10	10	1	b	5

[a] Semivolatile POHCs were not analyzed in integrated gas samples.

[b] Volatile POHCs were not analyzed in Method 5 train samples.

TABLE J-14. RESULTS OF ANALYSIS OF DUPLICATE SAMPLES FOR METALS

	Waste feeds										
	Liquid portions				Solid portion		Persulfate impingers				
Analyte	WF(6)-1 (μg/g)	WF(G)-3 (μg/g)	WF(2)-6A (μg/g)	WF(2)-7B (μg/g)	WF(6)-1 (μg/g)	WF(6)-9 (μg/g)	M5(2)-2B (μg)	M5(2)-4A (μg)	M5(6)-6B (μg)	M5(6)-7A (μg)	M5(6)-8A (μg)
Ag	< 0.05/< 0.07	< 0.02/< 0.07	< 0.05/< 0.07	< 0.2/< 0.2	2.8/1.1	< 0.007/< 0.007					
As	4.5/4.2	5.2/5.0	4.8/5.4	3.7/4.1	36/18.1	< 0.02/< 0.02	< 2.0/< 2.0	< 5.5/< 1.1	< 3.2/< 3.2	< 1.4/< 1.4	< 1.5/< 1/5
Ba	0.4/0.7	1.2/0.7	1.3/1.1	93/120	2,200/990	2,500/3,400					
Be	< 0.07/< 0.07	< 0.07/< 0.07	< 0.07/< 0.07	< 0.07/< 0.07	< 3.0/< 4.2	< 0.3/< 0.3					
Cd	24/14	11/8.2	9.2/7.9	4.3/4.7	100/40	18/19					
Cr	69/60	89/67	120/99	150/170	2,400/900	1,400/2,100					
Hg	1.2/0.9	1.1/1.4	1.1/1.4	1.8/2.1	14/5.4	11/14	< 0.5/< 0.5	< 0.5/< 0.5	< 0.8/< 0.8	< 0.1/< 0.1	< 1.1/< 0.9
Ni	16/6.8	7.3/5.7	8.0/6.9	18/19	70/18	86/83					
Pb	550/330	580/380	1,300/900	570/670	10,000/4,000	7,500/9,900					
Sb	28/18	16/14	30/24	43/40	230/90	260/200					
Se	6.3/7.9	3.0/64	1.5/7.5	4.6/5.9	30/15	< 0.03/< 0.03	< 6.3/< 6.3	< 7.0/< 7.1	< 10/< 10	< 5.3/< 5.3	< 5.9/< 5.9
Tl	1.0/1.0	2.0/1.5	2.7/2.3	2.3/2.6	4.4/14	< 0.04/< 0.04					

TABLE J-15. RECOVERY OF METALS IN FORTIFIED WASTE FEED SAMPLES

	Liquid fraction								Solid fraction			
	WF(6)-1		WF(G)-3		WF(2)-6B		WF(G)-9		WF(6)-3		WF(6)-8	
Element	Spiking level (μg/g)	Percent[a] recovery	Spiking level (μg/g)	Percent[a] recovery	Spiking level (μg/g)	Percent[a] recovery	Spiking level (μg/g)	Percent[a] recovery	Spiking level (μg/g)	Percent[a] recovery	Spiking level (μg/g)	Percent[a] recovery
Ag	247	b	230	b	319	b	80	b	230	b	1,800	b
As	247	78	230	59	319	57	80	76	230	77	360	34
Ba	247	88	230	81	319	63	80	80	230	c	1,800	c
Be	247	74	230	56	319	54	80	71	230	86	360	33
Cd	247	72	230	49	319	52	80	70	230	89	1,800	c
Cr	247	70	230	58	319	39	80	73	230	c	1,800	c
Hg	247	67	230	56	319	50	80	66	230	89	360	42
Ni	247	75	230	59	319	55	80	75	230	87	360	29
Pb	247	87	230	36	319	c	80	86	230	c	1,800	c
Sb	247	65	230	45	319	50	80	c	230	113	1,800	90
Se	247	104	230	83	319	75	80	100	230	88	360	c
Tl	247	77	230	63	319	57	80	84	230	86	360	38

[a] Results of single analysis.

[b] Silver was not recovered in any samples. This may have been due to precipitation of the silver as AgCl.

[c] Fortification level was too low.

TABLE J-16. RECOVERY OF METALS IN FORTIFIED PERSULFATE IMPINGER SOLUTIONS FROM METHOD 5 TRAINS

	M5(6)-1B		M5(6)-3A		M5(2)-5A		M5(2)-8A		M5(2)-9A	
Element	Spiking level (μg)	Percent[a,b] recovery	Spiking level (μg)	Percent[a,b] recovery	Spiking level (μg)	Percent[a,b] recovery	Spiking level (μg)	Percent[a,b] recovery	Spiking level (μg)	Percent[a,b] recovery
As	30	101	20	117	10	101	10	85	20	100
Hg	50	82	75	98	50	89	50	105	25	91
Se	30	31	20	21	10	44	10	108	20	99

[a] Results of single determination by AAS.

[b] Percent recovery = $\frac{\text{Concentration in fortified sample - Concentration in unfortified sample}}{\text{Spiking level}} \times 100$

Method Blanks--

Method blanks, using all reagent chemicals and procedures used to prepare samples, were prepared for every 15 samples analyzed for metals. No unexpected contaminants were detected in the method blanks which could have affected the sample results.

Blind Samples--

Blind samples were submitted by the MRI QA Manager for analysis of metals just as for the POHCs. However, no EPA samples were analyzed. The results of these analyses are discussed in Appendix I.

Detection Limits--

Table J-17 lists the estimated detection limits for metals in the three matrices analyzed. The detection limit estimates were based on instrumental response, sample background, sample preparation methods and percent recoveries.

Comparison of Solid Digestion Procedures--

The results of the sealed ampule digestion and the Teflon bomb method are compared in Tables J-18 and J-19. The Teflon bomb method yielded slightly better recoveries and detection limit values, as well as generally higher results. Additionally, as shown in Table J-20, the Teflon bomb method seemed to digest the sample more completely than the sealed ampule method. Weighing of residues after digestion indicated that the Teflon bomb method achieved approximately 90 to 95% digestion compared to 45 to 55% digestion with the sealed ampule method. Due to the recalcitrant nature of these samples, the Teflon bomb was the more suitable method of decomposition since the bomb can endure more rigorous digestion conditions (i.e., greater internal pressures).

The conclusion from these data is that the Parr Teflon bomb provides more complete digestion and should be used for digesting solid wastes for future incineration experiments.

TABLE J-17. ESTIMATED DETECTION LIMITS FOR METALS

Analyte	Sample type: Waste feeds: Liquid phase (μg/g)	Sample type: Waste feeds: Solids phase (μg/g)	Sample type: Ammonium persulfate impinger samples (μg/ml)
Ag	0.07	0.021	
As	0.019	0.058	0.021
Ba	0.010	0.008	
Be	0.070	0.030	
Cd	0.007	0.001	
Cr	0.005	0.034	
Hg	0.010	0.032	0.025
Ni	0.007	0.031	
Pb	0.017	0.026	
Sb	0.050	0.055	
Se	0.050	0.132	0.03
Tl	0.030	0.025	

TABLE J-18. COMPARISON OF TEFLON BOMB AND SEALED AMPULE EXTRACTION TECHNIQUE FOR THE SOLID WASTE FEED FRACTIONS (μg/g)

	Metal					
	Ag		As		Ba	
	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule
WF(6)1	2.76	< 2.5	35.8	10.8	2,160	61.0
WF(6)2	2.78	< 2.5	21.9	17.2	3,600	91.0
WF(6)3	1.89	< 2.5	30.0	12.0	1,580	134.0
WF(6)4	2.52	< 2.5	31.7	< 1.9	1,280	379.0
WF(6)5	1.22	< 2.5	5.50	14.2	312	325.0
WF(6)6	1.90	< 2.5	26.8	10.9	1,230	167.0

	Metal					
	Be		Cd		Cr	
	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule
WF(6)1	< 3.0	0.30	105	68.0	2,370	1,430
WF(6)2	< 0.30	< 1.2	79.0	62.0	2,390	1,700
WF(6)3	0.3	< 0.30	54.0	37.0	2,120	1,280
WF(6)4	< 0.30	< 0.30	60.1	38.0	2,400	1,550
WF(6)5	< 0.30	< 0.30	20.0	85.0	420	1,440
WF(6)6	< 0.30	< 0.3	52.0	40.0	1,940	1,250

TABLE J-19. COMPARISON OF TEFLON BOMB AND SEALED AMPULE EXTRACTION TECHNIQUE FOR THE SOLID WASTE FEED FRACTIONS (μg/g)

	Metal					
	Hg		Ni		Pb	
	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule
WF(6)1	14.0	6.16	70.0	< 35	10,300	3,590
WF(6)2	16.0	7.28	44.0	< 35	11,300	5,760
WF(6)3	13.0	5.84	86.0	< 35	7,850	4,230
WF(6)4	14.7	5.89	137	< 35	89,140	5,370
WF(6)5	4.30	6.60	113	< 35	801	5,560
WF(6)6	12.0	5.35	159	< 35	1,660	4,620

	Metal					
	Sb		Se		Tl	
	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule	Teflon bomb	Sealed ampule
WF(6)1	226	162	30.0	4.57	440	13.5
WF(6)2	418	246	< 8.8	2.43	3.30	23.2
WF(6)3	129	119	35.0	4.75	28.0	12.5
WF(6)4	274	156	46.4	8.68	27.4	13.8
WF(6)5	68	116	28.0	8.26	2.30	16.1
WF(6)6	173	89	22.0	2.35	24.0	10.5

TABLE J-20. COMPARISON OF TEFLON BOMB AND SEALED AMPULE EXTRACTION TECHNIQUE FOR RECOVERY OF FORTIFIED METALS FROM THE SOLID WASTE FEED FRACTION

	Sample (% recovery)	
	Teflon bomb[a] WF(6)-3	Sealed ampule[a] WF(6)-2
Ag	b	b
As	77	61
Ba	b	b
Be	86	90
Cd	89	60
Cr	b	b
Hg	89	85
Ni	87	b
Pb	b	b
Sb	113	b
Se	88	b
Tl	86	b

[a] Samples fortified at 230 μg/g.

[b] Fortification too low to be detected.

APPENDIX K

DESCRIPTION OF ANALYSIS METHODS AND RECOMMENDED CHANGES IN SAMPLING/ANALYSIS PROTOCOLS

This appendix describes the techniques used to analyze the different types of samples generated on this program. Where appropriate, we have referenced the A. D. Little Manual method number(K-1).* However, it must be pointed out that the A. D. Little Manual does not provide sufficient details for the methods to be followed by a chemical technician. Generally, additional references need to be checked in order to obtain a full description of the method. For example, purgeable organics are analyzed according to A. D. Little Method A101, the details of which are contained in EPA Method 624. Although A. D. Little Method A101 b and c allude to the fact that non-water soluble samples need to first be dispersed in polyethylene glycol and then added to water for analysis by the purge-trap-desorb technique, the details of this procedure are not in the literature, but were available for this program because one of the personnel was involved in the initial development of the method. As another example, the method of gas bag and bulb analysis is not described in the A. D. Little manual, and specific procedures were developed and applied by MRI to perform the analyses.

Work carried out on this project to analyze the numerous samples identified a number of problems and resulted in several recommended changes in the protocol. These recommendations are presented on page 234 of this Appendix.

WASTE FEED ANALYSIS METHODS

Preparation of Waste Feed Samples for Aliquoting and Analysis

Prior to aliquoting the waste feed samples for analysis at MRI, or for sending samples to Rockwell for duplicate analysis, the samples were homogenized as well as possible using manual mixing techniques. The samples, contained in 1-qt screw-capped glass jars with Teflon® liners, were first homogenized by vigorous shaking (loss of volatiles should not occur readily for samples consisting of an organic matrix). The cap was then removed from the sample container and the sample stirred vigorously for about 15 sec with a heavy glass stirring rod. Half of the sample was then immediately poured into another clean sample container to yield an equivalent sample for Rockwell.

Since some layering of the samples may occur after the samples are divided, the samples were rehomogenized using the procedures described above just prior to removing an aliquot for analysis.

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* References cited in this Appendix are on page 239.

Organic Analyses

Volatiles--

The waste feed samples were analyzed using a method based on A. D. Little Method A101b for waste samples which are not soluble in water. A 1.0-g aliquot of the mixed waste feed sample was dispersed in 40 ml of prepurified polyethylene glycol (PEG). A 40-µl aliquot of the PEG solution was spiked into 5.0 ml of reagent water along with 100 ng each of a three-component internal standard (equivalent to 100 µg/g each in the original sample). The sample was then analyzed by the purge-trap-desorb technique as described in A. D. Little Method A101a.

Semivolatiles--

The solvent extraction of the waste feed samples was performed according to A. D. Little Method P023 in which a liquid waste sample is simply diluted with methylene chloride. A 5-g portion of the mixed waste feed sample was diluted to 100 ml with methylene chloride and dispersed with vigorous shaking. Anhydrous sodium sulfate was added to bind the water present. A 1-ml aliquot of the diluted sample was spiked with 20 µg of D_{10}-anthracene internal standard (equivalent to 400 µg/g in the original sample). The sample was then analyzed by GC/MS with a fused silica capillary column according to A. D. Little Method A121. Since the waste was simply diluted, the acidic compounds such as phenols would also be present in the sample. Phenols are analyzed according to A. D. Little Method A111 which is similar to A121 except for the GC temperature programming conditions.

For samples which gave saturated peaks using the above method, an additional dilution of the sample was performed, and the diluted sample spiked with internal standard and analyzed. If only purgeable compound spectra from early in the chromatogram were saturated, a reanalysis for semivolatiles was not performed because the purgeable compounds were more accurately quantified using A. D. Little Method A101b. Prior to selection of the final list of POHCs for this program, the data were searched for as many compounds on the potential POHC list as possible using a reverse library search routine. For sample WF(6)-2, the mass spectra of all compounds in the sample were examined and as many as possible were identified as described in A. D. Little Method A016. The quantification of compounds for which no calibration standard was available was performed by dividing the RIC area counts of the enhanced mass spectrum of the analyte peak by the RIC area counts of the enhanced mass spectrum of the internal standard and multiplying by the concentration of the internal standard.

Metals--

The metals in the waste feed samples were digested according to Method P032. However, the method was modified so that the digestion of the solid fraction of the waste took place inside a pressured container. Both the Parr Teflon bomb and a sealed glass ampule(K-2) were evaluated as described below.

The waste feed samples were first separated into a liquid fraction and a solid fraction using centrifugation. The solid fraction made up about 10% by volume of the sample.

Approximately 1 g of the liquid fraction of the sample was digested in a covered beaker with 20 ml of concentrated ultrapure nitric acid at 90°C. The digested sample was then filtered through No. 42 Whatman filter paper and diluted to a final volume of 10.0 ml with 8 N (50%) nitric acid.

To digest the solid samples, 0.5 g of solid was placed in the bottom of acid-cleaned 20 mm x 145 mm Pyrex test tubes. Five milliliters of 10% ultrapure HNO_3 were then added to each sample and the tubes were placed in a hot-air oven at 60°C for approximately 22 hr, after which the temperature was raised to 125°C for 3 hr. The sample tubes were then removed, cooled, and inspected to ensure the presence of liquid acid. The tube sides were reinforced with adhesive tape and flame-sealed to provide air-tight pressure vessels. The sample tubes were then placed inside a sealed metal container and heated for 1 hr at 125°C in a hot-air oven. Immediately prior to opening, the sample tubes were super-cooled in liquid nitrogen to reduce any internal gas pressure to less than one atmosphere. The sealed tubes were then scored with a file; the nick was moistened with deionized water and touched immediately with a white-hot gas rod. The samples were filtered through No. 42 Whatman filter paper and diluted to 20 ml with 50% nitric acid.

The Teflon Parr bomb digestion method consisted of weighing 0.1 to 0.2 g solid waste feed sample into acid-cleaned Teflon bomb cups, adding 3 ml of 50% nitric acid, sealing the cups in steel sleeves and heating for 5 hr at 125°C in a hot-air oven. After the samples cooled overnight, the contents of the bomb cup were filtered and diluted to 10 ml final volume with 50% nitric acid.

The samples were analyzed for the volatile metals by atomic absorption spectrophotometry (AAS). Arsenic was analyzed by A. D. Little Method A222, selenium by A. D. Little Method 231, and mercury by A. D. Little Method A228.

Inductively coupled plasma (ICP) atomic emission spectrometry was used to screen digested waste feeds for additional metals and to check atomic absorption spectrophotometric analyses of impinger samples. The analytes of interest for the waste feed samples were Ag, As, Ba, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se and Tl.

A representative sample of the waste feed digests was scanned about the emission peaks of the 12 analyte elements to determine spectral interferences. The following spectral interferences were corrected during quantification by appropriate modification to the computer programs:

Ag	No interferences
As	Al baseline shift
Ba	No interferences
Be	Fe spectral overlap
Cd	No interferences
Cr	No interferences
Hg	No interferences
Ni	No interferences

Pb	No interferences
Sb	Sn spectral overlap
Se	Ca spectral overlap
Tl	Fe spectral overlap, Ti and Al baseline shift

After calibration, each sample was aspirated into the spray chamber-ICP torch assembly for 30 sec prior to performing quantitative analysis. Two 10-sec emission sampling periods were used to determine the analyte concentrations.

All instrument parameters and generated data files were recorded. The following instrument parameters were used:

Forward Power (kw): 1.1
Reflected Power (w): 2
Observation Height (mm): 20
Nebulizer Type: FCF
(FCF = Fixed crossflow)
(HS = High solids)

Coolant Gas Flow (ℓ/min): 18
Plasma Gas Flow (ℓ/min): 0.1
Sample Gas Flow (ℓ/min): 0.5
Solution Uptake (ml/min): 1.6
Peristaltic Pump Used?: yes

These are typical instrument settings for analysis of aqueous samples. The use of the peristaltic pump improved precision and reduced the likelihood of nebulizer plugging.

MODIFIED METHOD 5 TRAIN AND INTEGRATED GAS BAG ANALYSIS METHODS

The modified Method 5 train sample components consisted of a particulate filter, XAD-2 resin adsorbent trap, condensate water, probe rinses, and persulfate impinger solution. The filter, XAD-2 resin, condensate water, and probe rinses were analyzed for semivolatile POHCs; the persulfate impinger solution for metals. The gas bag samples were analyzed for volatile POHCs and PICs according to the methods described below.

Semivolatile POHCs in MM5 Samples

Particulate Filters--

The Method 5 train filters were Soxhlet extracted overnight as described in A. D. Little Method P024b, except that the solvent was benzene, rather than methylene chloride, so that the samples would be more amenable to analysis with an on-column injector used for subsequent GC/MS analysis.

XAD-2 Resins--

The XAD-2 resins were extremely wet from the aqueous condensate passing through the XAD-2 resin trap. The resin first had to be washed with a water-miscible solvent which would remove the water from the resin, yet allow recovery of any POHCs removed from the resin in the washing step. An azeotropic 3:1 mixture of benzene/methanol was used for this purpose. The XAD-2 resin was then extracted overnight with additional 3:1 benzene/methanol as described in A. D. Little Method P024b. The benzene/methanol-water from the washing step and Soxhlet extraction step were combined and shaken to extract any POHCs from the methanol-water phase into the benzene phase. The two phases were separated and the benzene layer concentrated using Kuderna-Danish evaporation. The XAD-2 resin blanks were Soxhlet extracted with benzene only.

Subsequent to the analysis effort, MRI learned from EPA that methylene chloride should have been used instead of benzene/methanol in the extraction step. Since there were no samples left, an experiment was conducted later on in the laboratory to evaluate the recoveries with the two procedures. Methylene chloride did yield higher recoveries as shown in the table below.

TABLE K-1. RECOVERY OF POHCs FROM SPIKED XAD

Compound	Dry XAD/CH_2Cl_2	Wet XAD/CH_2Cl_2	Wet XAD/benzene-methanol
Pentachloroethane	66	14	0.5
1,3-Dichlorobenzene	72	65	55
1,4-Dichlorobenzene	76	67	62
1,2-Dichlorobenzene	69	64	55
Hexachloroethane	57	68	47
Hexachlorocyclopentadiene	77	89	42
Hexachlorobenzene	89	78	83

As shown in Table K-1, the results indicated that methylene chloride gave better recoveries for most of the POHCs. In comparing the methylene chloride and benzene-methanol extraction efficiencies from wet resin, the methylene chloride yielded slightly higher recoveries for 1,3-, 1,4-, and 1,2-dichlorobenzene, and significantly higher recoveries for hexachloroethane and hexachlorocyclopentadiene. Pentachloroethane was recovered poorly with both solvents and was almost totally lost; however, pentachlorobenzene may be analyzed as a volatile compound from VOST and gas bag samples. Benzene-methanol gave a slightly higher recovery for hexachlorobenzene. Moreover, the effect of wet XAD resin on recoveries of POHCs by methylene chloride is shown in the first two columns of data in Table K-1.

Condensate Water--

The condensate which was collected in the Method 5 samples was extracted at pH > 11 for neutral and basic compounds as described in A. D. Little Method P021a.

Probe Rinses--

The probe rinse samples consisted of a mixture of water, acetone, and cyclohexane. The samples separated into a top cyclohexane layer and a bottom acetone-water layer. The cyclohexane was separated and used for subsequent POHC analysis.

Combination and Concentration of Train Sample Extracts--

With the exception of samples M5(6)-5B and M5(6)-8B, the extracts from each of the components of the Method 5 sampling trains were combined prior to POHC analysis. Each component of the Method 5 sampling train for samples M5(6)-5B and M5(6)-8B were analyzed separately for POHCs. The extracts were dried with sodium sulfate and concentrated using Kuderna-Danish concentration according to A. D. Little Method P031. However, final concentration to 1 ml was made under a stream of nitrogen at ambient temperature, rather than by heating with a 2-ball microsnyder column as described in A. D. Little Method P031. This ambient temperature concentration yields better recoveries according to our experience on other programs and the experience of researchers at Research Triangle Institute (see EPA Contract No. 68-03-2704 report - Master Scheme for the Analysis of Organic Compounds in Water - Part III)(K-3).

During concentration, insoluble matter occassionally condensed out of the extract. This material seemed to be extracted from the Method 5 filters, and was similar in appearance to the particulate matter originally collected on the filter. When this condensate appeared, the extract was filtered through glass wool and the concentration continued. This material could not be identified using direct insertion probe MS.

Integrated Gas Samples

Volatile POHCs were sampled using Tedlar bags. Stainless steel bulbs were also used in Runs 7-9. The contents of these containers were analyzed by first drawing the contents through a 1/4 in. x 10 cm stainless steel tube containing approximately 0.25 g of Tenax GC. This tube was then immediately transferred to the gas chromatograph/mass spectrometer where it was thermally desorbed using a Bendix thermal desorption apparatus and analyzed as described in A. D. Little Method A101. Five hundred milliliter portions of samples IGS-5 and IGS-6 were analyzed by packed column GC/MS as described in Method A101. Five liter portions of samples IGS-1, IGS-3, IGS-4, IGS-7 and IGS-9 were also analyzed as described in Method A101, but with cryogenic trapping using liquid nitrogen on a capillary SE-54 column to achieve better resolution and a lower detection limit.

Volatile Metals in MM5 Train Samples

The ammonium persulfate/silver nitrate impinger solutions, which were used to sample volatile metals in stack effluents, were analyzed according to the procedures described in Reference K-4 of this appendix.

To prepare the samples, 25-ml aliquots of the impinger solutions were refluxed with 5 ml of concentrated ultrapure nitric acid and 1 ml of ultrapure sulfuric acid (H_2SO_4). The solutions were cooled and transferred to a

50-ml graduated cylinder. Twenty milliliters of concentrated ultrapure hydrochloric acid were added to the solutions, and the total digest volume was brought to 50 ml with deionized water.

ADDITIONAL SAMPLES

Scrubber Effluents

The scrubber effluent samples were analyzed for both volatile and semivolatile POHCs. Semivolatile POHCs were extracted using the procedure described in A. D. Little Method P021a for basic and neutral organics and analyzed by GC/MS using Method A121. The volatile POHCs were analyzed by purge-trap-desorb GC/MS using A. D. Little Method A101a.

Bottom Ash

The samples which were identified as "bottom ash" were actually aqueous samples which contained less than 1% solids by volume. Consequently, these samples were analyzed for POHCs using methods for aqueous samples rather than for solids. The semivolatile POHCs were extracted using A. D. Little Method P021a for basic and neutral organics and analyzed using Method A121. The volatile POHCs were analyzed by purge-trap-desorb GC/MS using A. D. Little Method A101a.

Fuel Oil

The fuel oil samples were analyzed for volatile and semivolatile POHCs using exactly the same procedures as described for the waste feed samples above.

GC/MS CONDITIONS

Semivolatile POHCs

Semivolatile POHCs were analyzed by GC/MS using two different instruments. The extracts of the aqueous scrubber effluent, bottom ash, and make-up water samples as well as the dilutions of the waste feed and fuel oil samples were analyzed on a Finnigan 4000 GC/MS with an INCOS data system. The extracts from the Method 5 sampling train components were analyzed using a Varian 2700 gas chromatograph interfaced with a Varian 311A mass spectrometer with an INCOS data system. Both instruments were equipped with 15 m x 0.25 mm ID SE-54 fused silica capillary columns from J&W.

Two microliter portions of the aqueous sample extracts, fuel oils and waste feed dilutions in methylene chloride were analyzed on the Finnigan 4000. The GC/MS instrumental conditions were:

Injector: Grob-type split/splitless (from Finnigan)
Column temperature: 40°C (hold for 4 min) to 325°C at 10°C/min
Injector temperature: 250°C
Injector split ratio: 0.5
Vent time: 1.5 min
Mass scan range: *m/z* = 40 to 475
Scan rate: 1 sec

One microliter aliquot of the Method 5 train extracts in benzene were analyzed on the Varian 2700/Varian 311A system. The GC/MS instrumental conditions were:

Injector: J&W on-column capillary injector
Column temperature: 80°C (4-min hold) to 325°C at 10°C/min
Detector temperature: 295°C
Ion source temperature: 270°C
Mass scan range: *m/z* = 45 to 475
Scan rate: 1.5 sec
Ionization energy: 70 eV; 0.6 ma

Volatile (Purgeable) POHCs

The purge-trap-desorb analyses of aqueous samples were performed on a Varian 3700 GC interfaced with a Varian CH4 magnetic mass spectrometer. The following GC/MS conditions were used:

Column: 6 ft x 2 mm ID glass column packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopak C
Column temperature: 40°C (3-min hold) to 175°C at 8°C/min
Ion source temperature: 250°C
Mass scan range: *m/z* = 40 to 255
Scan rate: 3 sec
Ionization energy: 70 eV

Volatile POHCs (Integrated Gas Samples)

The gas samples were transferred from the collection device (gas bag or bulb) to a Tenax trap. The adsorbed compounds were then thermally desorbed into the GC/MS system using a Bendix flasher.

Samples IGS-5 and IGS-6 were analyzed on the Varian 3700 GC/Varian CH4 MS used for the purge-trap-desorb analyses. The GC/MS conditions were as follows:

Column: 6 ft x 2 mm glass with 0.2% Carbowax 1500 on 80/100
Carbopak C
Column temperature: 40°C (3-min hold) to 175°C at 8°C/min
Flasher temperature: 200°C
Desorption time: 6 min
Ion source temperature: 250°C
Mass scan range: m/z = 40 to 255
Scan rate: 3 sec
Ionization energy: 70 eV

The integrated gas samples from tests 1, 3, 4, 7 and 9 were analyzed on the Finnigan 4000 GC/MS. For these analyses, the contents of the Tenax tubes were desorbed onto a 15 m by 0.25 mm SE-54 fused silica capillary column. To retain the desorbed volatile POHCs, the first few centimeters of the column were immersed in a liquid nitrogen bath. Following desorption, the liquid nitrogen was removed and the chromatographic analysis was started. The GC/MS conditions were as follows:

Column: 15 m x 0.25 mm fused silica coated with SE-54
Column temperature: 30°C (4-min hold) to 250°C at 10°C/min
Flasher temperature: 200°C
Desorption time: 6 min
Ion source temperature: 250°C
Mass scan range: m/z = 40 to 475
Scan rate: 1 sec
Ionization energy: 70 eV

RECOMMENDED CHANGES IN THE SAMPLING AND ANALYSIS PROTOCOLS

Discussed below are details of some of the problems encountered with analyzing the components of the Modified Method 5 sampling train and waste feed samples along with recommended changes in the analytical procedures for future incineration tests.

Improvements in the Waste Feed Analysis Procedures

There have been several improvements in the analytical methods for waste feed types of samples since the A. D. Little manual was compiled. For example, in a method currently being tested in an interlaboratory validation study conducted by Battelle Columbus Laboratories for EPA-EMSL/Las Vegas and in which MRI is participating, the pH of the sample is tested so that the sample taken for analysis can be buffered with a phosphate buffer and extracted at neutral pH to increase the extraction efficiency of acidic and basic compounds. (This is used for samples which cannot be simply diluted with solvent.) The method also incorporates solvent extraction using ultrasonification which ensures complete extraction and homogenization of any solid or particulate material in the hazardous waste samples.

Homogenization of Bulk Waste Feed Samples

A problem that has not been adequately addressed at this point is the homogenization of bulk hazardous waste samples prior to removing aliquots for analysis. For this program, every effort was made to homogenize the samples using manual shaking and stirring techniques. However, for liquid samples which contain two or three separate phases, including an aqueous phase, more rigorous homogenization techniques may be needed. The good precision and accuracy achieved for the analysis of MRI and EPA QA blind samples suggests that any lack of precision associated with duplicate analyses of waste feed samples may reflect differences in the composition of the sample aliquots rather than a problem with the determinative GC/MS analysis step.

Alternatively, the sample aliquots may have been equivalent, but yielded different analytical results due to an unknown matrix effect of the sample itself.

If more rigorous homogenization of the samples is needed, some mixing techniques that may be quite useful for homogenizing bulk samples of hazardous waste might be mixing the waste sample in a Waring blender or high shear type of apparatus.

Use of Direct Adsorption for Collection of Volatile POHCs--

The analysis of the integrated gas samples provided some analytical difficulties. The principal problem was that some of the gas bags leaked most or all of the sample. Also, since the gas concentrations were relatively low, the contents of the bag and bulk samples had to be concentrated. Only if the concentrations are quite high in the samples can a gas sampling valve or gas tight syringe be used to introduce the sample into the mass spectrometer. For example, if the concentration of the POHC in the waste is 100 $\mu g/g$, the concentration in the effluent at 99.99% DRE is only about 1 $\mu g/m^3$ or 1 ng/liter. To inject 500 ml of this sample (0.5 ng) with a gas-tight syringe (the largest size available) onto a GC column with a 30 ml/min flow rate would be impractical.

The concentration technique that was used for the integrated gas samples was to concentrate the components of the gas bag or bulb onto a Tenax adsorbent trap and then heat-desorb the compounds with a gas flow into the GC/MS for analysis.

Tenax is a common air sampling adsorbent that has been evaluated against other porous polymer adsorbents in various air sampling scenarios. Under stack sampling conditions in the Modified Method 5 train Tenax is not as useful as XAD-2 because of its lower capacity (more rapid breakthrough). However, in contrast to the Tenax, the XAD must be solvent extracted to remove the organic components.

The ideal air sampling adsorbent for analysis of volatiles should have a large capacity at ambient temperature (large adsorption constant) for low molecular weight compounds yet allow complete desorption of the sample components by heating (small adsorption constant at the desorption temperature used for the highest molecular weight compounds of interest)(K-5). Tenax is commonly used for air sampling, although Porapak Q has been shown to provide superior sampling capacity for low molecular weight halogenated organics and also allows rapid heat desorption of volatile organic compounds. Tenax, along with smaller amounts of silica gel and, in some cases activated charcoal, is the adsorbent commonly used to trap volatile organic compounds purged from water for subsequent desorption with heat and analysis by gas chromatography with a specific detector, i.e., electron capture detector or mass spectrometer (A. D. Little Method A101). The flow rate through the adsorbent trap for these analyses is 40 ml/min for 12 min (480 ml total). The silica gel and charcoal may be added to the trap to collect extremely volatile and polar compounds such as vinyl chloride or freons wich may break through the Tenax. Silica gel and charcoal also trap a considerable amount of water. Since the entire sample is analyzed at one time using the heat desorption technique, in contrast to the solvent extraction used with XAD-2, the amount of material in the sample required for analysis is very small, e.g., only a few nanograms can easily be detected.

Thus, it is recommended that volatile POHCs in the stack gas be sampled by collecting the gases directly onto an adsorbent trap at the sampling site. A separate train could be used such as the one used to collect gases for SO_2 analysis (EPA Method 6). The sample could be collected at a flow rate of about 100 ml/min for 20 min (2 liters) to provide a composite sample on Tenax which is then transferred to a test tube with a Teflon-lined screw cap and returned to the laboratory for analysis. Breakthrough of volatile organic components from the trap should only occur if the stack effluent components are present at very high concentrations (i.e., several tens of micrograms). This technique should provide sufficient sensitivity to determine DREs for the volatile POHCs of interest. At the time of this report, an alternate sampling train is being evaluated for volatile organics under EPA sponsorship.

A summary of the expected advantages of using Tenax adsorption, rather than gas bulb or bag sampling, to analyze stack effluents are listed below.

- An adsorbent trap is much smaller and easier to handle than gas bags.

- After collection the adsorbent trap can be stored by simply placing it into a screw-cap test tube and capping tightly.

- None of the sample components are lost due to leaks as can easily occur with the gas bags. Also, none of the components of the sample are lost to the walls of the container.

- The adsorbent traps are analyzed by simply inserting the trap into a heat desorption unit interfaced to the analytical system, e.g., GC/MS. The samples may be stored up to several weeks without change in the composition of the samples.

- Sampling could be done at a lower flow rate, to provide an integrated sample that coincides with the MM5 sampling train.

In contrast to the difficulties in spiking solid matrices with semivolatile POHCs, Tenax adsorbent traps can be readily spiked with internal and surrogate standards in order to quantify the amount of each compound of interest collected in the sample. A few microliters (mg) of each of the desired standards is first added to a glass bulb of known volume which can be sealed with a silicone septum. The added compounds are vaporized inside the bulb, with the aid of warming, if required, and the concentration of the added compounds in the bulb determined from the weight added and the total volume of the bulb. Thus, a known amount of each standard compound can be removed by withdrawing the appropriate volume (generally a few microliters) into a gas tight syringe and injecting the gaseous sample into the center of the adsorbent trap just prior to analysis. This technique has been successfully used on a number of projects and was used on this project to spike the Tenax traps onto which the components of the sampling bulbs and bags were collected.

Spiking of Solid Sample Matrices

An area of concern in POHC analysis is how to determine the extraction efficiency of POHCs from solid sample matrices, i.e., the air particulate filters and the XAD-2 adsorbent resin. Common spiking techniques for solids do not simulate the mechanism by which the compounds are actually collected, i.e., by filtration of particulates on air particulate filters or by adsorption onto the XAD-2 resin. There does not appear to be any particular problem in recovering compounds collected on filters or XAD-2 resins using exhaustive Soxhlet extraction. However, it is believed that there is a problem in trying to demonstrate good recovery by the use of surrogate spiking procedures prior to extraction.

Tests were performed in which a particulate filter was spiked with a solvent solution of the POHCs to determine the extraction efficiency. Most of the POHCs were found to evaporate almost immediately along with the solvent. This is not unexpected considering the volatility of the chlorinated ethanes, dichlorobenzenes, and hexachlorocyclopentadiene. Only the least volatile of the POHCs, hexachlorobenzene, showed good recovery efficiency. Problems were also evident in spiking and recovering POHCs from spiked XAD-2 resin, again probably due to evaporative losses of POHC compounds as the solvent evaporated.

The A. D. Little Method Manual addresses the spiking of aqueous samples, but not solid samples. If spike recovery data from solid samples is desirable, then an appropriate spiking procedure needs to be developed and evaluated.

Spiking of Aqueous Samples

The QA data on percent recoveries of the surrogate compound (decafluorobiphenyl) and the selected POHCs from aqueous samples fortified with these compounds were very low. If low recoveries are reproducible, they may be acceptable because the amount of a compound found in a sample can be divided by the average percent recovery to give the amount of the compound actually present in the sample. However, a review of QA data generated on some other projects revealed variable recoveries of fortified compounds from reagent water. It is very important, therefore, to determine the cause of low recoveries from aqueous matrices, and also to take steps to maximize recovery. All of the semivolatile compounds selected as POHCs for this program, except for hexachlorobenzene, are quite volatile and would be expected to volatilize to some extent during concentration of the methylene chloride extract. On future incineration studies, it will be important to supplement the recovery data obtained from fortification of POHCs into aqueous matrices with recovery data from fortifying reagent water samples followed by extraction, concentration, and analysis, and also data from simply fortifying an aliquot of the solvent followed by concentration and analysis. In this way, matrix effects, poor extraction efficiency, and evaporative losses can all be distinguished. Unfortunately, not enough of this type of data were generated for this program to determine the principal cause(s) of the low recoveries found by MRI for the POHCs; and similar low recoveries reported by Rockwell for surrogates.

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